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CATION METASOMATIC REPLACEMENT REACTIONS

L. L. AMES, JR.[1]

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ABSTRACT

The principles governing cation replacement reactions were investigated utilizing reactions between calcium-, strontium-, and barium-containing solutions and the minerals calcite-strontium-witherite and gypsum-celestite-barite. Results indicated that both the replacement order and rates of replacement are directly related to the difference in solubility between the original column material and final replacement product. Replacement rates approach zero as the ratio of the concentration of the two cations in the altering solution approaches the activity ratio of the two cation-common anion compounds. For example, Sr^{+2} from solution may replace Ca^{+2} of calcite only until the $\frac{^aCaCO_3}{^aSrCO_3}$ is approached by buildup of Ca^{+2} concentration in solution.

Changes in the composition of solutions causing replacement reactions both with time and distance from sources are the rule rather than the exception for multi-minerallic deposits.

INTRODUCTION

SEVERAL anion replacement systems involving minerals with a common cation were previously investigated in the laboratory (1, 2, 3, 4). It is the

[1] General Electric Company, Richland, Washington. Work performed under Contract No. AT (45-1)-1350 for the U. S. Atomic Energy Commission.

purpose of this paper to investigate replacement reactions that proceed between minerals having a common anion, including gypsum-celestite-barite and calcite-strontianite-witherite. The above mineral associations are characteristically found in two geochemical environs: 1) low-temperature hydrothermal, as gangue minerals in sulfide veins or as bedded replacement products in limestones and marls (5, 6, 7, 8, 10), and 2) normal sedimentary environs, as a result of circulation of meteoric waters containing the cations Ca^{+2}, Sr^{+2}, and Ba^{+2} (5, 6, 7, 8, 10). The experimental conditions of this study are directly applicable to parts of the latter environment, and should at least give a first indication of the mineral relationships prevalent in the former.

METHODS OF INVESTIGATION

The experimental apparatus used here was similar to that described previously (1). Fifty-gram columns of starting mineral were placed in a constant temperature bath. Influent solutions containing appropriate cations were passed through the columns using a constant-head pump calibrated to deliver standardized flow rates. Samples of the influent and effluent solutions were collected and sent to the Analytical Laboratory of the Hanford Laboratories operation for radioanalysis. From these analyses, the concentration of radioisotope tracer, and hence the traced macroconstituent, in the influent and effluent was known. The fraction of radioisotope retained on the column could then be computed. By holding all independent variables except one at some arbitrary value, relative reaction rates may be obtained by observation of the dependent variable, the fraction of radioisotope removed.

To obtain data on the phases in a kinetic system with a given influent solution at 60° C the solution was pumped through three grams of reagent grade starting material contained in a chromatographic tube.

All products were identified by their X-ray diffraction patterns. Chemicals used in makeup of solutions were reagent grade in distilled water. The high specific activity Sr^{85} and Ba^{133} were obtained from Oak Ridge in the form of chlorides.

Photomicrographs of replacements of $CaCO_3$ by $BaCO_3$, $CaCO_3$ by $SrCO_3$ and $CaSO_4 \cdot 2H_2O$ by $SrSO_4$ were obtained by immersion of the starting materials in 0.1*M* solutions of appropriate cation for two months, and preparing thin sections of the altered material.

RESULTS

Figure 1 shows a photomicrograph of replacement of a calcite rhomb by witherite, and Figure 2 is a replacement of calcite by strontianite. In the latter case, much of the $SrCO_3$ replacement layer was removed during cutting and grinding of the thin section. Figure 3 is a photomicrograph of the replacement of a gypsum cleavage plate by celestite. Alteration to celestite was essentially complete. Note the celestite rosettes and common twinning that were not present in the original gypsum. Alteration of a similar gypsum plate to barite was relatively rapid. The resulting photomicrograph

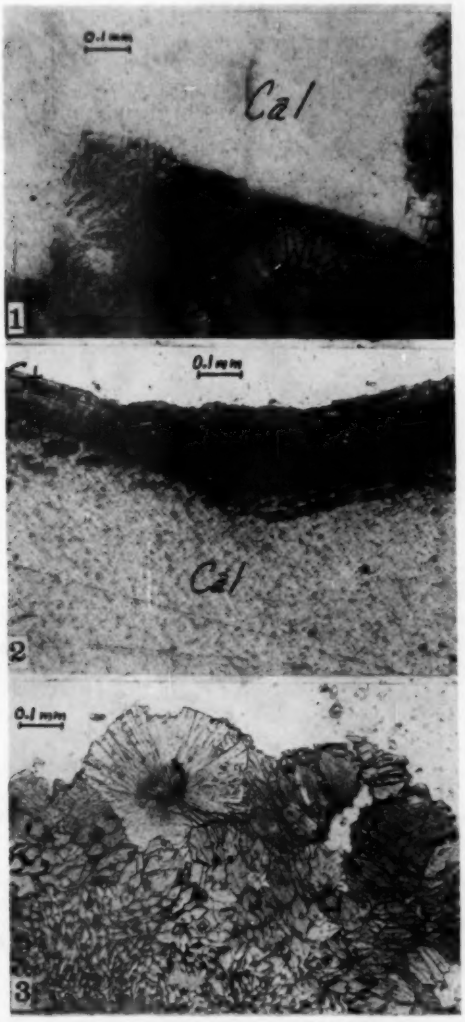

FIG. 1. Photomicrograph of a thin section showing witherite replacement of calcite. Cal—calcite; Wi—witherite.
FIG. 2. Photomicrograph of a thin section showing strontianite replacement of calcite. Cal—calcite; St—strontianite.
FIG. 3. Photomicrograph of a thin section showing complete celestite replacement of a gypsum cleavage plate.

was composed of a very fine-grained barite, however, and showed little of interest.

Figure 4 is a graph of the cation fraction retained on the solid vs. temperature. The original column material is noted in each case along with the reacting cation and radiotracer present in the influent solution. Note that a concentration of 1*M* NaCl was common to all influent solutions to

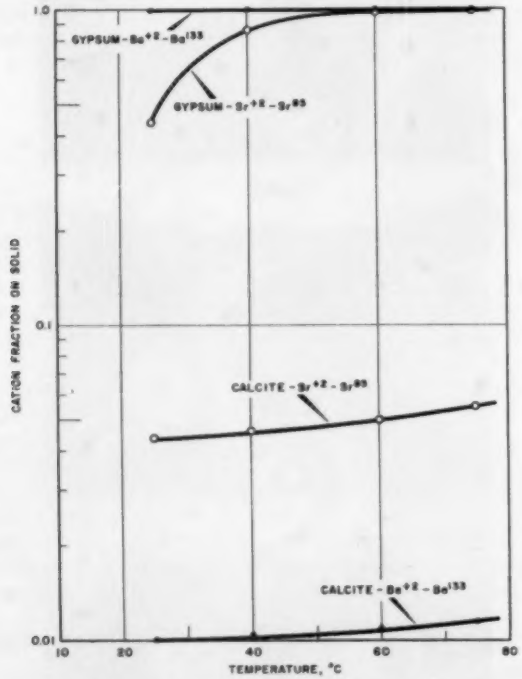

FIG. 4. A comparison of the order of replacement of several cation replacement reactions. Influent solution, 1*M* NaCl, 0.05*M* other active macroconstituents and radiotracers as indicated; Influent *p*H, 5.0; Common flow rate, 410 ml/cm²/hr; Temperature, as indicated; Column, 50 g of calcite or gypsum as indicated; Surface areas, 0.067 m²/g.

duplicate more closely the natural geochemical environs mentioned in the introduction.

Table I lists examples of the phase relations prevalent in certain open systems in which cation replacement reactions occur. Closed system results, starting under the same system conditions, often lead to erroneous conclusions as to phase reltionships. For example, the treatment of gypsum and calcite with $BaCl_2$ solution eventually leads to barite and witherite as the final products in an open system. In a closed system, however, the altera-

tion of $CaCO_3$ to $BaCO_3$ does not occur because of an increase of Ca^{+2} and depletion of Ba^{+2} in the altering solution as a result of the relatively rapid replacement of gypsum by barite. One might erroneously consider $CaCO_3$ stable in the presence of $BaCl_2$ in an open system from a study of these data.

DISCUSSION

For the purposes of this paper, four cation replacement reactions were studied. The chemical equations for these reactions may be written as follows:

1) $CaCO_3 + BaCl_2 \rightleftharpoons BaCO_3 + CaCl_2$

2) $CaCO_3 + SrCl_2 \rightleftharpoons SrCO_3 + CaCl_2$

3) $CaSO_4 \cdot 2H_2O + BaCl_2 \rightleftharpoons BaSO_4 + CaCl_2 + 2H_2O$

4) $CaSO_4 \cdot 2H_2O + SrCl_2 \rightleftharpoons SrSO_4 + CaCl_2 + 2H_2O.$

Table I presents several interesting column results in which the above reactions occur. As with the anion replacement reactions, only one final product is stable in a system containing the constituents for two possible

TABLE I

KINETIC PHASE RELATIONS IN SOME CATION–SULFATE AND CATION–CARBONATE SYSTEMS

Influent solution	Original column material	Final product
0.03*M* $SrCl_2$	gypsum	celestite
0.03*M* $SrCl_2$	calcite	strontianite
0.03*M* $BaCl_2$	gypsum	barite
0.03*M* $BaCl_2$	calcite	witherite
0.03*M* $MgCl_2$	gypsum	gypsum
0.03*M* $MgCl_2$	calcite	calcite
0.03*M* $BaCl_2$	gypsum + calcite	barite + witherite
0.03*M* $BaCl_2$	gypsum + celestite	barite
0.03*M* $BaCl_2$ 0.03*M* $SrCl_2$ 0.03*M* $CaCl_2$	gypsum	barite
0.03*M* $BaCl_2$ 0.03*M* $SrCl_2$ 0.03*M* $CaCl_2$ 0.03*M* $MgCl_2$	calcite	strontianite
0.03*M* $BaCl_2$ 0.03*M* $SrCl_2$ 0.03*M* $CaCl_2$ 0.03*M* $MgCl_2$	gypsum	barite

final products with a common anion, both less soluble than the original column material. As an example, when an influent containing equal concentrations of Ba^{+2} and Sr^{+2} is passed through gypsum, only barite is finally stable in the system. The case of mixed initial column material reacting with a single cation is also of interest. For example, the reaction of an influent containing Ba^{+2} with an initial column of gypsum plus celestite re-

sulted in a barite final product. Results of partial alterations of the mixed original column material showed that the rate of reaction between gypsum and $BaCl_2$ was much more rapid than between celestite and $BaCl_2$. When a column of gypsum plus calcite was altered by a Ba^{+2} solution, the calcite persisted until the alteration of gypsum to barite was nearly completed. Then the alteration of calcite to witherite began.

The two alteration stages may be explained on the basis of the relationship of reaction rates to differences in solubility between an initial column material and a final product. Table II shows the cation replacement relationships that should prevail if the order of replacement is a function of relative solubility and the replacement rates are determined by solubility. Given a common anion, the cation that allows the least concentration of anion in that solution should prevail in the formation of a chemical compound. As can be seen from the data presented in Figure 4 and Table II, the rate and order of cation replacements are directly related to the difference in solubility between starting mineral and final mineral product. In other words, starting with a common anion, the proportion of the two cations

TABLE II

SULFATE AND CARBONATE SOLUBILITY DATA AT 25° C AND ONE ATMOSPHERE PRESSURE ASSUMING 0.03 MOLAR CATION CONCENTRATIONS

Mineral	Activity product (9)	Mg^{+2}	Ca^{+2}	Sr^{+2}	Ba^{+2}	SO_4^{-2}	CO_3^{-2}
Gypsum	3.6×10^{-5}	—	3.0×10^{-2}	—	—	1.5×10^{-3}	—
Celestite	7.6×10^{-7}	—	—	3.0×10^{-2}	—	2.5×10^{-5}	—
Barite	1.5×10^{-9}	—	—	—	3.0×10^{-2}	5.0×10^{-8}	—
Calcite	4.7×10^{-9}	—	3.0×10^{-2}	—	—	—	1.6×10^{-7}
Strontianite	6.9×10^{-10}	—	—	3.0×10^{-2}	—	—	2.3×10^{-8}
Witherite	1.6×10^{-9}	—	—	—	3.0×10^{-2}	—	5.3×10^{-8}
Magnesite	7.9×10^{-6}	3.0×10^{-2}	—	—	—	—	2.7×10^{-3}

remaining in solution should be the same as the ratio of the activity products of the two minerals formed by the cations and common anion. The activity data are obviously not rigorously correct, especially with $1M$ NaCl present, but general relationships are nevertheless indicated as valid. For example, the removal rate of Sr^{+2} as strontianite by reaction with calcite is considerably greater than the corresponding removal of Ba^{+2} as witherite. From Table II, the concentration of CO_3^{-2} in equilibrium with Ba^{+2} and witherite is 5.3×10^{-8} molar and with Sr^{+2} and strontianite, 2.3×10^{-8} molar. Consequently strontianite, with the same cation concentration, allows less common anion in solution than witherite. Thus activity ratios may be used not only to determine the order of replacements, but also their relative rates of replacement. It should be emphasized, however, that little if anything of the whole solution composition can be inferred from activity ratios and the minerals comprising the deposit.

Let a solution containing equal concentrations of Ba^{+2} and Sr^{+2} be passed through a gypsum bed. The applicable activity products are 7.6×10^{-7} for celestite, 1.5×10^{-9} for barite and 3.6×10^{-5} for gypsum.

Hence the only stable final replacement product of the gypsum is barite. During the replacement reaction, the reaction rate approaches zero as the activity ratio of Ca^{+2} to Ba^{+2} approaches $\frac{3.6 \times 10^{-5}}{1.5 \times 10^{-9}}$ or 2.4×10^{4}, assuming that the solution-solid system obeys Raoult's law. As this ratio already is considerably greater than that wich would allow the replacement of gypsum by celestite, the celestite replacement reaction does not occur. The final result is that as the solution containing the original concentration of Sr^{+2}, more Ca^{+2} and less Ba^{+2} flows through the gypusm bed, the rate of barite formation approaches zero. This solution is then in equilibrium with the gypsum despite its high Sr^{+2} concentration. It would be impossible to ascertain whether or not such an altering solution contained Sr^{+2} from a consideration of the minerals in the resulting deposit (barite and gypsum) and the applicable activity product constants.

To illustrate some of these reactions with hypothetical activities, a solution containing $0.03M$ Sr^{+2}, $0.03M$ Ba^{+2} and $1.3 \times 10^{-6}M$ Ca^{+2} is passed through a bed of gypsum. Barite replaces gypsum during solution passage until the ratio of Ca^{+2} to Ba^{+2} approaches 2.4×10^{4}, or until the concentration of Ba^{+2} falls to a limit of $1.3 \times 10^{-6}M$ while Ca^{+2} increases to $0.03M$. At this point in its passage through the gypsum, the solution contains approximately $0.03M$ Sr^{+2}, $0.03M$ Ca^{+2} and $1.3 \times 10^{-6}M$ Ba^{+2} and is, for all practical purposes, at equilibrium with the gypsum bed. From this point, the solution will thus pass on through the gypsum bed without further reaction or change in composition.

In the case of alteration of a mixed gypsum and celestite bed by a $0.03M$ Ba^{+2} solution, the activity ratios governing replacement rates are $\frac{a_{SrSO_4}}{a_{BaSO_4}} = 5.0 \times 10^{2}$ and $\frac{a_{CaSO_4 \cdot 2H_2O}}{a_{BaSO_4}} = 2.4 \times 10^{4}$. The gypsum alters to barite more rapidly than celestite to barite.

Furthermore, the celestite to barite replacement ceases when the Ba^{+2} concentration decreases to $6.0 \times 10^{-3}M$ from $3.00 \times 10^{-2}M$. Alteration of the gypsum to barite by the solution continues as the solution moves down the column until the Ba^{+2} concentration theoretically approaches $2.5 \times 10^{-7}M$. In practice there is initially very little, if any, celestite and much more gypsum replaced by barite due to the large differential between Ba^{+2} removal rates. The front marked by nearly complete alteration of gypsum to barite considerably precedes in time and space the alteration of celestite to barite.

Considering one more reaction type, a mixed bed of calcite and gypsum are altered by a solution containing $0.03M$ Ba^{+2} and $1.3 \times 10^{-6}M$ Ca^{+2}. As the concentration of Ba^{+2} falls to $1.0 \times 10^{-2}M$, the replacement of calcite by witherite ceases, while replacement of gypsum by barite continues until the concentration of Ca^{+2} is $3.0 \times 10^{-2}M$ and Ba^{+2} is $1.3 \times 10^{-6}M$. The alteration of gypsum to barite considerably precedes in time and space the alteration of calcite to witherite.

With several anions such as fluoride, carbonate, and phosphate also present, the replacement situation becomes increasingly complex although

the same solubility criteria govern these as well as all other replacement reactions.

We have considered here only the principal driving force of replacement reactions, that of a solubility difference between original mineral and final replacement product. Though temperature, influent pH, column flow rate, surface area of original mineral, and active cation concentration do not, of themselves, actuate replacement reactions, these system conditions certainly effect the rate at which the replacement proceeds. The relationship between these system variables and the removal rates of tracing cations and anions require further study.

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Feb. 20, 1961

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GEOCHEMICAL PROSPECTING FOR NICKEL IN THE BLUE MOUNTAIN AREA, JAMAICA, W.I.

V. G. HILL

ABSTRACT

Geochemical prospecting investigations in the serpentine area near Cedar Valley indicate that in the vicinity of Arntully-Woburn Lawn there is a zone where the concentration of nickel is between 0.2–0.3%. The nickel is associated with magnetite, which contains between 0.2 to 0.5% nickel but some is also present as nickelian serpentine.

INTRODUCTION

A SERIES of exposures of nickel bearing serpentine occur near Cedar Valley on the St. Thomas side of the Blue Mountain Range and extend from the vicinity of Penlyne Castle to near Serge Island. The largest of these extends from Penlyne Castle to near Cedar Valley, although it is partially covered by overlying sediments.

The terrain is rugged, with the slope varying from precipitous to gentle, and the elevation between 1,750 to 3,280 feet above sea level. The principal rivers are the Negro and Stony Valley rivers, tributaries of the Yallahs river, but there are also a number of seasonal streams. About two-thirds of the area is cultivated and the remaining portion is covered by forests and secondary growth. Road connection to Kingston is via Morant Bay or Llandewey.

Most of the field work was done during the period September to November 1959.

GEOLOGY

The geology of the area is not fully known, but the current mapping by the Geological Survey Department should furnish additional detail. In outline the geology is simple, but it is extremely complex in detail. Speaking broadly it appears that an ultrabasic sill, probably a laccolith, intruded along a fault and accommodated itself between the purple conglomerate and the shaly beds. The zone of contact metamorphism is observed up to approximately fifty feet wide, and in this zone the shales are indurated and chloritized. The host sediments contain off-shoots of the intrusive, and partially transformed xenoliths of the sediments are found in the intrusive. The rocks in the lower conglomerate group are probably even more affected than the overlying shales, and the limestone has been changed to marble. The intrusive is approximately 900 feet thick in the Arntully-Woburn Lawn area, but it thins out fairly rapidly especially in the direction of Cedar Valley. It has now been almost completely transformed to serpentine, chlorite and

actinolite, and has a bronzite rich zone in the vicinity of Ness Castle. Burns (1) examined a specimen[1] from this area and showed it to have a

typical serpentine structure with small areas (0.3 mm) of serpophite[2] enclosed by fibrous aggregates of antigorite. This antigorite-serpophite assemblage is traversed by narrow vein-like developments of magnetite. Small patches of disseminated magnetite grains also occur. Bronzite occurs as phenocrysts throughout the rock. There is no marked development of schiller structure in these crystals. Small grains of residual olivine are scattered throughout the rock, generally within the antigorite-serpophite assemblage but occasionally enclosed by bronzite phenocrysts. Phenocrysts of opaque minerals occur up to 2 mm in size. These appear in most cases to be magnetite but at least one grain of chromite occurs. No evidence of shearing is seen on microscopic examination but several of the bronzite crystals are fractured or bent.

The chemical analysis of the above specimen is given in Table 1.

Figure 1 shows the outline of the major serpentinite outcrops. This map is generalized and the contact zone between serpentinite and the host sedi-

TABLE 1

CHEMICAL ANALYSIS OF SERPENTINITE FROM NESS CASTLE

Constituent	Wt. percent
SiO_2	38.2
Al_2O_3	2.8
TiO_2	0.18
Fe_2O_3	5.2
FeO	1.4
MgO	38.2
CaO	1.2
MnO	0.14
Na_2O	0.14
K_2O	0.07
P_2O_5	0.12
H_2O	12.8
Cr_2O_3	0.17
CO_2	Tr
NiO	Not determined
Total	100.6

Analyst: D. Burns.

ments is gradational. The areas shown as serpentinite contain small overlying remnants of shale but these are omitted. The largest of these is near Arntully. It is believed that these major serpentinized bodies are continuous but this has not been proven. Both the sediments and the basic intrusive are later cut by an acid dike that runs from beyond Arntully house through Ness Castle to Brooklands. There are a number of offshoots of this main type.

Soils.—The removal of the forest cover from most of the region, and the extremely steep slopes have facilitated the erosion of the soil. The fracturing of the serpentine has also contributed to soil creep, landslides, and erosion especially as the rainfall is seasonal and often torrential. The result of all this is that today the serpentinite zone is almost devoid of soil cover. In the areas covered by sediments the problem is less acute.

[1] Specimen collected by V. A. Zans in vicinity of Ness Castle, St. Thomas.
[2] A compact variety of serpentine.

A layer of black to red top soil of an average thickness of about six inches and a range of zero to three feet deep rests directly on the weathered substratum in the serpentinite area. This zone is generally gray in color, and consists of serpentinized and partially serpentinized fragments in a fine-grained matrix. The packing appears to be random.

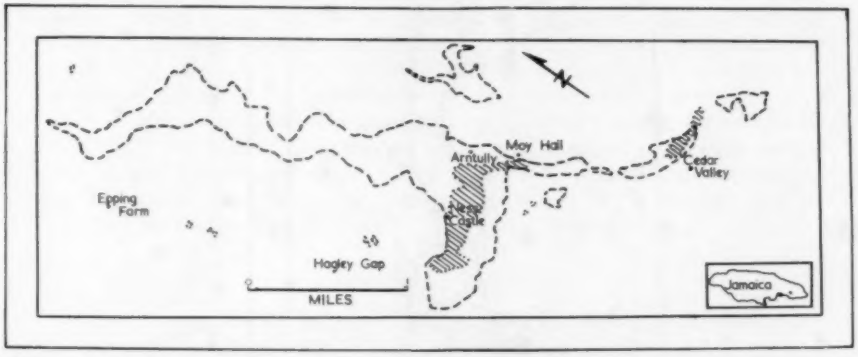

FIG. 1. Map of the Cedar Valley area showing the location of the major serpentine outcrops, and areas where there is an anomalous concentration of nickel. (Geological data based on provisional map supplied by the Geological Survey Department, Jamaica.)

SAMPLING

The object of the preliminary survey was to delineate those areas where there is a significant concentration of nickel in the soil. It was decided to use a simple and rapid sampling technique because the terrain is rugged and it is extremely difficult to follow a grid. Samples were therefore collected along roads and foot paths. River valleys are not particularly suitable because the concentration of nickel in the secondary zone that develops in the river deposits is of a different order of magnitude to that of the primary anomaly due to the nickel originally present in the rock, and so would tend to cause a bias in the distribution. The preliminary survey through the area indicated that the nickel is primarily associated with the gray weathered substratum developed in the serpentinite zone, and so apparent ambiguities in the data, as the presence of low values on the flood plains in the nickel-bearing serpentine, can be resolved when interprted against the background of the geology. The material sampled is potentially ore, and is not merely associated with an ore-bearing horizon so the results from these tests immediately indicate the grade of any possible ore present. This project is therefore different from most geochemical prospecting investigations where the material sampled is related to possible ore by an ion exchange reaction with the clays present.

Samples were from below the top soil, at a depth varying between six inches and four feet, but averaging about one foot, generally from the banks

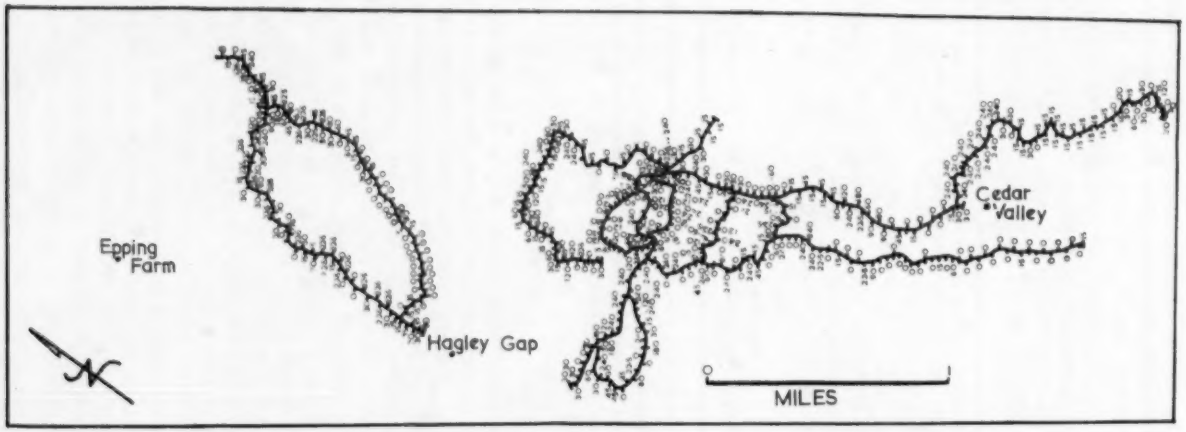

FIG. 2. Map of the Cedar Valley area showing the traverses made and the distribution of nickel values (multiply values by 10).

of roads and footpaths, but where this was impracticable, a small hole was dug to penetrate the top soil and the sample was taken from the bottom. The usual weight of sample taken was about 500 grams. This was placed in a numbered paper bag and its location was noted. The distance between sample points was 200 feet along the surface.

For convenience the sample points were located directly on aerial photographs (scale approximately 1/10,000). Key points with the associated sample numbers were marked on these photographs, and the intermediate points were plotted by interpolating between the key points. This technique is relatively simple, yet accurate enough for a survey of this type. One assistant and a laborer can collect approximately sixty samples daily.

Methods of Analysis.—The samples were dried in the bags for two hours at 90° C. The minus sixty mesh fraction was removed from each sample after it had been disaggregated. The fines were returned to the original bag and the rest was discarded. The nickel content of the samples was determined by the method outlined by Hill and Ellington (3).

RESULTS

The traverses and the relative nickel values of the soils and laterite samples are shown in Figure 2. The frequency distribution of nickel was determined by the technique described by Hill (2) and the cumulative and unique frequency curves are given in Figure 3. The unique frequency curve is bimodal with a background distribution mode at 300 ppm nickel (2.47 on the log scale) and an anomalous distribution mode at 2400 ppm nickel (3.38 on log scale). The cut off point for the anomalous distribution is 1600 ppm nickel (3.20 on log scale). A comparison of the distribution of nickel values in the serpentinite and soils associated with the serpentinite, with those for the other rock types and their associated soils is given in Table 2.

If the non-serpentinite rocks are assumed to represent the background distribution we can select $(\overline{X} + 3s)$ for these rocks as the level above which values are significant (i.e. 99.73% significance level). This gives a value of 3.27 on the log scale or 1,850 ppm nickel on conversion to the arithmetic value. This value is in agreement with that obtained from the unique frequency curve. A t-test on the means (log scale) for the serpentine compared to the other rock types shows that this difference in means is highly significant. The cut-off point of 1600 ppm, obtained from the unique frequency curve, was selected because it is felt that it is safer to include, rather than to reject, an area that is not significant. On this basis the areas containing anomalous values are delineated as shown in Figure 1. The principle anomaly is in the Arntully-Ness Castle area, and there is a subsidiary one north of Cedar Valley. The nickel content of the anomalous zones is between 0.2–0.3%.

The anomalous areas delineated in Figure 1 show well developed phenocrysts of bronzite, otherwise very little difference was observed in hand specimens from both areas of the serpentinite. Hand specimens of the serpentinite from anomalous areas, and the rest of the intrusive were tested for

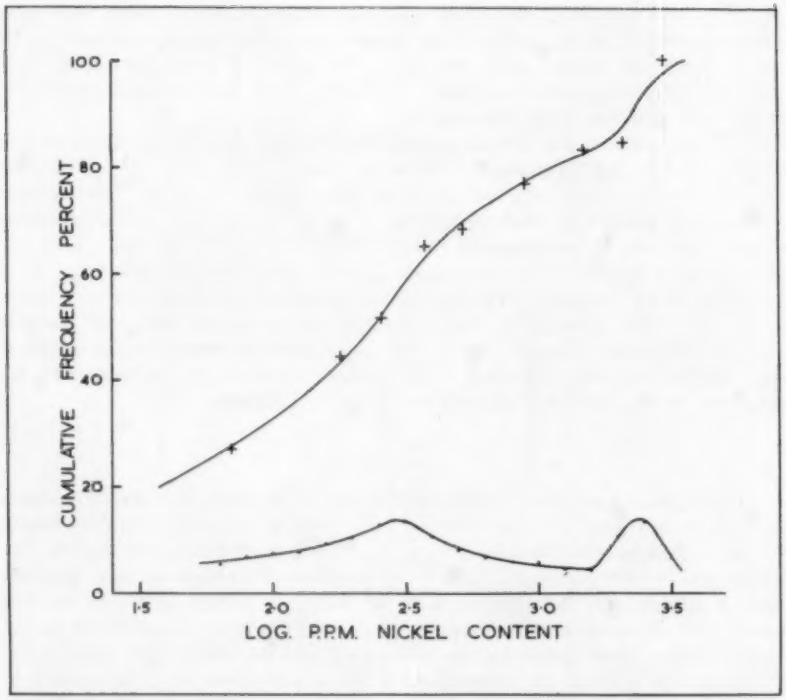

FIG. 3. Cumulative and unique frequency curves for the distribution of nickel values.

nickel by etching them in nitric acid fumes, neutralizing the acid with ammonia fumes, drying, and finally developing the nickel dimethylglyoxime color by spraying the surface with an alcoholic solution of dimethylglyoxime. It was found that the nickel is widely distributed in the matrix of the rock, but not in the bronzite phenocrysts. This would suggest that the nickel is either associated with the magnetite phase or substituted in the silicates

TABLE 2

COMPARISON OF NICKEL VALUES IN SOILS RELATED TO SERPENTINITE AND THAT FOR OTHER ROCK TYPES

Rock type	N	$\overline{X}$	Gm	s^2	s
Serpentinite	232	1,316	2.844	0.314	0.560
Other rocks	277	270	2.280	0.108	0.329
All rocks	509	801	2.537	0.201	0.453

N—Number of samples in group; $\overline{X}$—Arithmetic mean $\Sigma(\overline{X})/N$; Gm—Geometric mean, $\Sigma(\log X)/N$; s^2—Estimated variance, $\Sigma(X - \overline{X})^2/N$.

(nickel-bearing antigorite etc.) instead of occurring as distinct nickel minerals. Specimens from the anomalous areas were therefore separated into magnetic and non-magnetic fractions and tested for nickel. Table 3 shows these results.

These results suggest that nickel is present in the magnetite phase and that there is a rough relationship between nickel and magnetite content. The nickel content of the non-magnetic minerals increases with the magnetite content. The nickel present is probably substituted in the structure. Nickel bearing magnetite with 1.76 percent nickel has been reported (4) and nickelian antigorite is well known. The possibility that the nickel detected in the non-magnetic fraction is due to finely disseminated nickelian magnetite cannot be overlooked, although it is more than likely that nickel-bearing silicates are present.

A few samples of the soil and crumbly serpentine were sifted into the following fractions—6, 8, 10, 14, 18, 36, 44, 60, 85, 100, 150 mesh and the

TABLE 3

THE RELATIONSHIP BETWEEN MAGNETITE AND NICKEL CONTENT OF THE SERPENTINE

No.	% Nickel	% Magnetite	% Ni in magnetite	% Ni in other minerals
1	0	tr	N.D.	0
2	0.03	1.5	N.D.	0.03
3	0.12	4.5	N.D.	0.18
4	0.12	11.3	0.5	0.18
5	0.12	2.2	N.D.	0.12
6	0.24	20.4	0.5	0.24
7	0.24	12.2	0.2	0.18
8	0.24	14.4	0.5	0.12
9	0.24	25.4	0.4	0.24
10	0.03	2.4	N.D.	0.03

Tr = trace; N.D. = value not determined.

pan. All these fractions contained identical percentages of nickel as determined by the field method, supporting the hypothesis that the nickel is present as a solid solution in a widely distributed phase or phases rather than as a particular nickel mineral.

CONCLUSION

These results show that there is a nickel-rich facies, probably associated with the presence of bronzite phenocrysts in the serpentinite. The results further indicate that the nickel is present in solid solution in magnetite and some of the silicates. Magnetite is extremely resistant to weathering and this explains why there has been no residual concentration of nickel, particularly in the finer fraction. The nickel content in the magnetite is 0.2 to 0.5 percent, a value considered too low to warrant interest, because the added cost of crushing and concentration of the magnetite will undoubtedly make the whole process uneconomic at the present time.

The restricted nature of the anomalous zone is due either to the transformation of most of the intrusive to a hybrid rock by reaction with the host sediments, thereby lowering the average nickel content of the boundary zone of the mass, or that the intrusive was low in nickel which formed solid solution sulfide phases. Because the rock is serpentine, and probably derived by hydro-metamorphism of peridotite the possibility of alteration of primary nickeliferous sulfides to other minerals, including magnetite, is real. Nickel can be easily accommodated in the secondary hydrous silicates and in magnetite.

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SECONDARY GLAUCONITE IN THE BIWABIC IRON-FORMATION OF MINNESOTA

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ABSTRACT

Glauconite has been identified from six localities in the Precambrian Biwabic iron-formation of the Mesabi range. The appearance in thin section is that of a normal diagenetic alteration. The field occurrence suggests a secondary origin: (1) localization of the glauconite in the border zone between iron ore bodies and unoxidized iron-formation, (2) occurrence at different horizons within the iron-formation from one mine to the next, and (3) as cross-cutting fracture-fillings and in quartz and chalcedony veinlets. Confirmation of a secondary origin is given by K-Ar dates of 100 and 150 million years for two specimens. It is suggested that the glauconite formed when the Cretaceous sea covered the Precambrian terrane. The porous iron ore bodies at the surface were saturated with marine waters that reacted with unoxidized to partially oxidized iron-formation in the border zones and along fractures to form glauconite of Cretaceous age in a rock of Precambrian age. Glauconite-bearing Cretaceous sediments lie directly upon the Biwabic iron-formation at several localities. Failure of glauconite to form in Precambrian time is attributed either to absence of the proper salinity level or to lack of a favorable environmental oxidation potential.

The Mg contents of three analyzed specimens are comparable to that of the average marine glauconite, as determined from 52 analyses from the literature. The amount of tetrahedral substitution in two specimens is normal for marine glauconites but for a third specimen is lower, approaching that for non-marine occurrences. The iron-rich environment is reflected in unusually high ferric and ferrous iron contents, whereas the octahedral Al values and ferric/ferrous ratios are unusually low. A trend is noted towards increase in octahedral cation total with decrease in interlayer cation total.

OCCURRENCE

DURING a recent study of the clay-size accessory minerals associated with the Precambrian iron ores of the Lake Superior region (1), glauconite was identified by X-ray techniques from six localities on the Mesabi range—the Auburn, Gilbert, and Rouchleau mines in the Virginia area, the Hill Annex mine at Calumet, the Embarrass mine near Aurora, and the Siphon mine at Trimble, Minnesota.

The glauconite at the Auburn mine occurs in the transitional zone between the iron ore body and the unoxidized Lower Slaty member of the Biwabic iron-formation. Examination of drill core of unoxidized iron-formation peripheral to the ore body indicates that the glauconite is restricted to the border of the ore body and, therefore, does not follow a stratigraphic horizon in the iron-formation. The glauconite in the transitional zone is associated with both shale and granular chert. It occurs as thin laminae generally 1 to

3 mm in thickness and as disseminated sheafs of lath-shaped crystals in a buff to tan siliceous shale. The mineral has a deep bluish-green color and when wetted becomes soft and plastic. The glauconite in the granular chert occurs as lath-shaped crystals oriented perpendicular to the border and forming a partial to complete rim around the chert granules (Fig. 1). Some chert granules are almost completely replaced by radially oriented laths of glauconite. Chalcedony and quartz veinlets, which ramify through the granular chert, also contain sheafs of lath-shaped glauconite crystals. The glauconite in the granular chert is commonly altered to goethite with the preservation of the original sheaf-like texture, whereas the glauconite in the

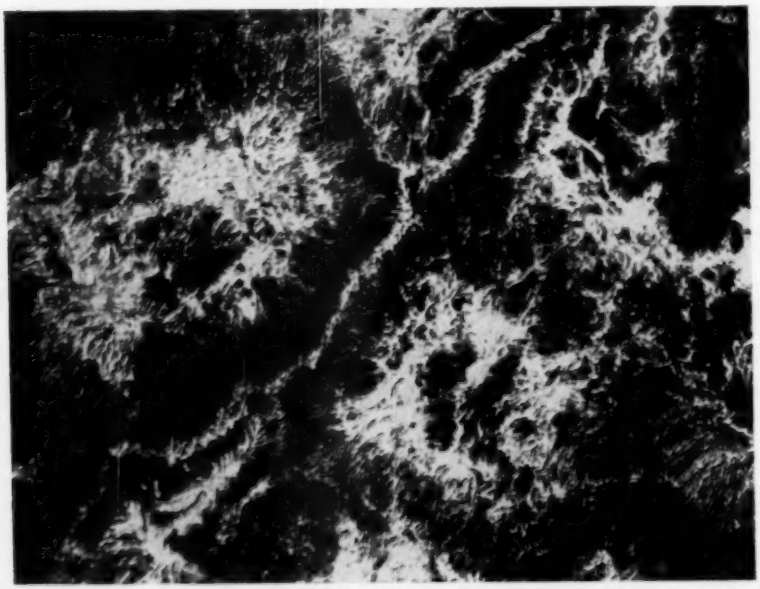

FIG. 1. Glauconite sheafs replacing the borders of chert granules in an apparent diagenetic alteration. Lower Slaty member of Biwabic iron-formation, Auburn mine, Minnesota. 100 ×.

quartz and chalcedony veinlets is relatively fresh and unaltered. Glauconite also occurs as fracture fillings.

The glauconite at the Gilbert mine occurs as fracture fillings and coatings in drill core of the Lower Slaty member of the iron-formation at a depth of 192 feet. The lath-shaped glauconite crystals are oriented perpendicular to the walls of fractures, but assume a more random sheaf-like habit away from the walls.

The mineral occurs at the Rouchleau mine as a fracture filling and also

in a disseminated state in areas adjacent to fractures in cherty minnesotaite-siderite iron-formation. The minnesotaite and siderite have been oxidized to goethite in a zone $\frac{1}{4}$ to $\frac{1}{2}$ inch in width adjacent to the glauconite-filled fracture. Disseminated sheafs of glauconite occur in this zone. Locally, goethite pseudomorphous after minnesotaite occurs beyond the border of the goethite zone in the minnesotaite-siderite iron-formation. The glauconite is intimately related and occurs adjacent to crystals, groups of crystals, and irregular masses of goethite in this zone.

At the Hill Annex mine near Calumet, Minnesota, the glauconite is present in the transitional zone between the iron ore body and the unoxidized Lower Cherty member of the Biwabic iron-formation. The occurrence is similar to that in the granular chert of the Auburn mine with the exception that the lath-shaped glauconite crystals show a more random distribution at the borders and within the chert granules.

The glauconite at the Embarrass mine occurs in the transitional zone between the ore body and the unoxidized iron-formation. The mineral is particularly abundant at the Lower Slaty horizon where it occurs primarily as fracture fillings.

At the Siphon mine glauconite occurs as fracture fillings in partially oxidized iron-formation peripheral to the ore body. The lath-shaped glauconite crystals, which are locally altered to goethite, are oriented perpendicular to the walls of the fractures.The iron-formation is composed of chert, magnetite, and minnesotaite. The minnesotaite in the vicinity of the fractures has a light brownish color suggesting that the iron is largely in the ferric state. Sheafs of lath-shaped glauconite occur in a disseminated manner in the areas of brownish minnesotaite.

MINERALOGY

X-ray study shows that all six occurrences of green glauconite-like minerals described in this paper are true glauconites.The patterns correspond to that of an iron-rich dioctahedral 1 M mica with d (060) varying between 1.510 and 1.515 Å, depending on iron content. The basal 001 reflections are fairly sharp and well defined. Solvation and heating tests indicate 5 to 15 percent expansible layers, with one specimen (Embarrass) having 25 percent.

Since the iron-formation represents an unusually iron-rich environment for glauconite occurrence, the resulting compositions are of considerable mineralogical interest. Three of the Mesabi glauconites and one specimen of an iron-bearing 1 M muscovite from the Gunflint district were purified by a combination of hand-picking under the binocular microscope, dispersion and sedimentation in water, magnetic separation, and heavy liquid centrifugation. Purification was continued until no impurities could be detected by X-ray study. Depending on the amount available after concentration, complete or partial analyses were obtained by gravimetric, colorimetric, and flame photometric methods. Total Fe contents were determined by X-ray spectography on all seven samples, two (Siphon and Hill Annex) being somewhat impure. The results are listed in Table 1.

The glauconite analyses were recast to structural formulas by the method of Marshall (24), assuming 22 cationic charges for one-half the unit cell.

$$\text{Rouchleau}\quad \left[\underbrace{(Al_{0.04}\ Ti_{0.04}\ Fe^{+3}_{1.23}\ Fe^{+2}_{0.43}\ Mg_{0.40})}_{2.14}\ \underbrace{(Si_{3.81}\ Al_{0.19})}_{4.00}O_{10}\ (OH)_2\right]^{-0.41-0.19-0.60}\ \underbrace{(K_{0.55}\ Na_{0.04}\ Ca/2_{0.01})}_{0.60}{}^{+0.61}$$

$$\text{Auburn}\quad \left[\underbrace{(Ti_{0.05}\ Fe^{+3}_{1.21}\ Fe^{+2}_{0.65}\ Mg_{0.33})}_{2.24}\ \underbrace{(Si_{3.71}\ Al_{0.13}\ Fe^{+3}_{0.16})}_{4.00}O_{10}\ (OH)_2\right]^{-0.25-0.29-0.54}\ \underbrace{(K_{0.51}\ Ca/2_{0.02})}_{0.53}{}^{+0.55}$$

$$\text{Gilbert}\quad \left[\underbrace{(Al_{0.37}\ Ti_{0.03}\ Fe^{+3}_{1.07}\ Fe^{+2}_{0.23}\ Mg_{0.51})}_{2.21}\ \underbrace{(Si_{3.63}\ Al_{0.37})}_{4.00}O_{10}\ (OH)_2\right]^{-0.10-0.37-0.47}\ \underbrace{(K_{0.41}\ Na_{0.05})}_{0.46}{}^{+0.46}$$

Two interesting features are noticeable in these formulas. The octahedral cations are in excess of the theoretical 2.00 total for a dioctahedral mica by 0.14 to 0.24 and the interlayer cation totals are 0.40 to 0.54 lower than the theoretical 1.00 value. Although water is not considered in this method of allocation, the water totals are higher than those of an ideal mica. The formula discrepancies and the interstratified expansible layers appear to be interrelated.

Analyses in the literature indicate a well-defined trend towards increase in octahedral cations with decrease in interlayer cations. This point is illus-

TABLE 1

	SiO_2	Al_2O_3	TiO_2	Total Fe	Fe_2O_3	FeO	MgO	CaO	K_2O	Na_2O	H_2O+
Rouchleau	51.45	2.59	0.67	20.76	21.99	6.92	3.62	0.07	5.84	0.27	5.63
Auburn	49.00	1.47	0.80	24.85	24.09	10.29	2.91	0.19	5.29	Tr	7.36
Gilbert	53.40	9.24	0.53	17.67	20.81	4.01	5.02	0.07	4.78	0.36	
Gunflint	49.32	20.92		5.38	2.75	4.45			8.66		
Embarrass				16.00							
Siphon				(23.20)							
Hill Annex				(18.50)							

trated in Figure 2 where the average octahedral and interlayer cation totals for 66 analyzed glauconites and celadonites are plotted. Average values are used here for interlayer and octahedral occupancy to decrease the effects from individual specimens of impurities and analysis errors, particularly the lack of flame photometry data for the alkalies in the older analyses. There is some evidence that for a given interlayer cation content non-marine celadonites tend to have higher octahedral cation totals than do marine glauconites. For the few analyses available of celadonites, however, the scatter of values is too large to enable a definite trend to be plotted. The glauconites and celadonites have been grouped together in Figure 2, with the positions of the average marine glauconite and of the average non-marine celadonite plotted for comparison.

One possible interpretation of the empirical trend observed in Figure 2 is that some of the cations allocated to octahedral sites actually belong in interlayer positions. Foster (14) has shown for several montmorillonites that octahedral cations in excess of the theoretical 2.00 value correlate closely with the cation exchange capacities observed for the same specimens. Allocation to the interlayer space of a percentage of the analyzed MgO content equivalent to the experimental cation-exchange capacity completely eliminates the excess octahedral total for these montmorillonites.

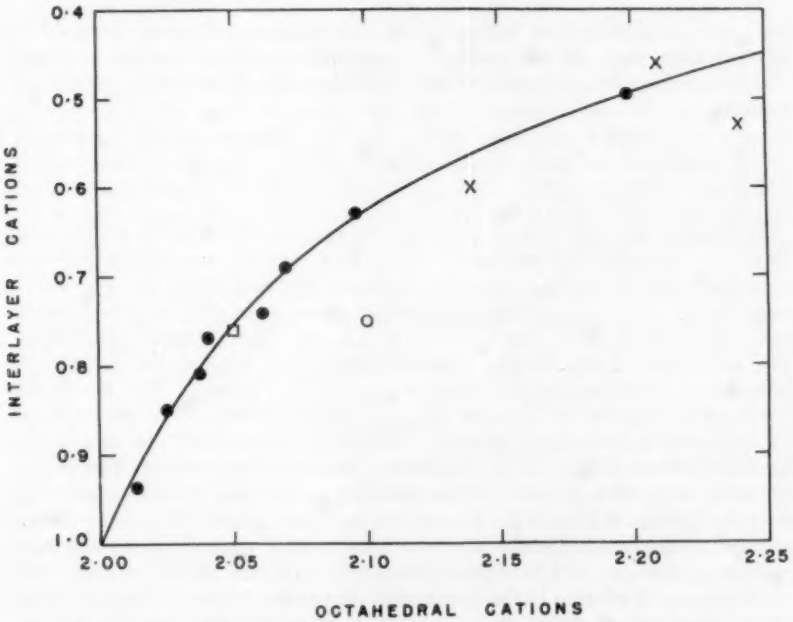

FIG. 2. Variation of average interlayer cation total with average octahedral cation total for 66 analyzed glauconites and celadonites. Data from the literature (2, 7, 13, 17, 20, 22, 23, 28, 30, 31) recalculated by the method used in this paper and divided into 8 approximately equal groups. The analyzed specimens of this paper are marked by crosses, the average marine glauconite by a square, and the average non-marine celadonite by an open circle.

Sufficient material was on hand for exchangeable Mg analysis on only one of the Biwabic glauconites. The Rouchleau specimen, after NH_4^+ saturation and three washings with 1 N ammonium acetate, yielded exchangeable Mg equivalent to 0.19 percent MgO. Allocation of this Mg to interlayer sites would reduce the octahedral cation total a minor amount from 2.14 to 2.12. Although additional analyses are desirable to check this point, the high octahedral totals appear to be real and not the result of the method of

allocation. Further study of the data from which Figure 2 was constructed shows that a decrease in interlayer charge tends to be compensated on the average by an increase in the octahedral sheet both in the total number of trivalent cations and in the ratio of trivalent to divalent cations.

The 52 marine glauconites included in Figure 2 yield an average structural formula

$$\overset{-0.44}{\underbrace{\left[(Al_{0.48}\ Fe^{+3}_{0.98}\ Fe^{+2}_{0.20}\ Mg_{0.39})_{2.05}\right.}}\ \overset{-0.36}{\underbrace{(Si_{3.64}\ Al_{0.36})_{4.00}}}\ O_{10}\ \overset{-0.80}{\underbrace{\left.(OH)_2\right]}}\ \overset{+0.80}{\underbrace{(K_{0.65}\ Na_{0.07}\ Ca/2_{0.04})_{0.76}}}.$$

This formula differs from that given by Hendricks and Ross (17), based on 32 specimens, only in the method of presentation of the interlayer cations. The 14 non-marine specimens included in Figure 2 yield an average structural formula

$$\overset{-0.65}{\underbrace{\left[(Al_{0.33}\ Fe^{+3}_{0.82}\ Fe^{+2}_{0.25}\ Mg_{0.70})_{2.10}\right.}}\ \overset{-0.17}{\underbrace{(Si_{3.83}\ Al_{0.16}\ Fe^{+3}_{0.01})_{4.00}}}\ O_{10}\ \overset{-0.82}{\underbrace{\left.(OH)_2\right]}}\ \overset{+0.81}{\underbrace{(K_{0.61}\ Na_{0.08}\ Ca/2_{0.06})_{0.75}}}.$$

This average formula utilizes 7 of the 10 analyses cited by Hendricks and Ross plus 7 additional analyses. The cation values are slightly different than those in the average formula of Hendricks and Ross, but the trends are similar. The non-marine specimens contain more Mg, less tetrahedral and octahedral Al, and a lower ferric/ferrous ratio than the marine specimens. The difference in Mg content between marine and non-marine occurrences is consistent in all but 1 of the 66 specimens used in Figure 2. The anomalous specimen is reported by Dyadchenko and Khatuntzeva (13) as occurring in a continental environment, replacing feldspar in alluvial and eluvial deposits near the Dnieper River. The composition, however, resembles that of marine occurrences in all respects. If this specimen is not taken into consideration, then the highest Mg value for the marine occurrences is 0.51 (corresponding to approximately 4.5 percent MgO) whereas the lowest value for the non-marine occurrences is 0.57 (approximately 5.3 percent MgO). There is a small amount of overlap in the tetrahedral Al values of the two environmental types, some part of which may be attributable to the difficulty of achieving complete separation of quartz from glauconite. Only 4 of the 52 marine glauconites have tetrahedral Al values less than 0.21 and only 1 non-marine specimen has a larger value (again excluding the Dnieper River specimen). Octahedral Al values and ferric/ferrous ratios, on the other hand, overlap a great deal and can not be considered diagnostic.

The three analyzed Biwabic specimens have Mg contents comparable to that of the average marine glauconite. The amount of tetrahedral substitution in the Auburn and Gilbert specimens is normal for marine glauconites, whereas the substitution in the Rouchleau specimen is lower and approaches that for non-marine occurrences. There is not enough Al present in the Auburn glauconite to fill the tetrahedral sites not occupied by Si, and it is necessary to place Fe in tetrahedral positions also. There is barely enough Al to fill the available tetrahedral sites in the Rouchleau specimen. Alloca-

tion of the analysis on the alternate basis of 12 anions instead of 22 cationic charges changes the cation equivalents sufficiently that Fe must also be used in tetrahedral sites for the Rouchleau specimen. In this connection Dekeyser (12) has claimed as a result of differential solution studies that it is necessary to have Fe^{+2} in tetrahedral sites to give a green color to glauconite. This substitution seems implausible because of the large size of Fe^{+2}, so we have allocated Fe^{+3} to tertahedral sites instead. Examples of Fe^{+3} in tetrahedral sites have been cited also by Sabatier (28) for a marine glauconite from the Pacific (original analysis by Collet) and by Schüller and Wohlmann (30) for a non-marine celadonite filling amygdules and fractures in a melaphyr.

The Biwabic glauconites reflect the iron-rich environment of the iron-formation by having unusually high ferric and ferrous iron contents with correspondingly low octahedral Al. The total Fe contents range from a maximum of 24.85 percent for the Auburn glauconite to a minimum of 16.00 percent for the Embarrass glauconite. The latter also contains the greatest percentage of expansible layers. The magnitude of the iron content is reflected conspicuously in the resulting color of the mineral, changing from light olive-green to dark blue-green with increasing Fe content. The ferric/ferrous ratios are low. All of the Biwabic glauconites contain small amounts of Mn, Cr, Ni, Ti, and Rb.

Partial analysis of the green 1 M muscovite from the Gunflint district indicates that it is phengitic but does not contain enough iron to be classified as glauconite. It has less than 5 percent expansible layers and nearly a full complement of interlayer cations.

GENESIS

The glauconite in the granular cherts of the Biwabic iron-formation replaces the chert granules in a manner suggestive of a diagenetic alteration (Fig. 1). However the field occurrence, (1) localization of the glauconite in the transitional zones between iron ore bodies and unoxidized iron-formation, (2) in cross-cutting fractures and in quartz and chalcedony veinlets, and (3) occurrence at different horizons within the iron-formation from one mine to the next, suggests either that the period of glauconite formation may be related to the period of ore formation or that the glauconite is later than both the iron-formation and the iron ore.

Specimens of glauconite from the Auburn mine and the Hill Annex mine were submitted to Dr. P. M. Hurley for K-Ar age determination. Hurley et al. (18, p. 121) report an age of 104 million years for the glauconite from the Auburn mine and 150 million years for the glauconite from the Hill Annex mine. According to the time scale of Hurley et al. (18, p. 109) the Auburn glauconite is Cretaceous in age and the Hill Annex glauconite is early Jurassic in age. Thus the K-Ar age determinations support the field evidence to the extent that they indicate the glauconite to be younger than the Precambrian Biwabic iron-formation. It seems unlikely from field evidence that these Mesozoic ages are also those of the iron ores. It is possible that the measured ages are average values and that the glauconite has formed

epigenetically over a long period of geologic time but this is not supported by the composition, which suggests a marine origin.

A Cretaceous age for the glauconite at the Auburn mine is not inconsistent with the regional geology of the Mesabi range. The present land surface is believed to be essentially the surface in contact with the Cretaceous sea, and the glauconite occurs within 200 feet of this surface for the 6 occurrences noted in this paper. Cretaceous shales, sands, and gravels, some of which are fossiliferous and others glauconite-bearing, lie directly upon the Biwabic iron-formation and are exposed in mines from Coleraine to Virginia and Eveleth. These sediments have been assigned by Bergquist (3) to the Coleraine formation and upon the basis of the invertebrate fauna are considered the age equivalent of the lower Benton of Colorado. The coarser clastics, much of which are unfossiliferous, are considered to be of fresh water origin. The abundance of ore pebbles in the basal Cretaceous conglomerates and the abundance of fine-grained hematite in the shales indicate that the iron ore bodies were in existence and subject to erosion in Coleraine time. Thus we can visualize the Cretaceous sea advancing over the Precambrian terrane of the Mesabi range—the porous iron ore bodies becoming saturated with marine waters that reacted with the unoxidized to partially oxidized iron-formation in the transitional zone and along fractures to form glauconite of Cretaceous age in a rock of Precambrian age.

A Jurassic age (150 million years) for the Hill Annex glauconite is somewhat surprising since no confirmed marine Jurassic deposits are known in the entire Mesabi area, whereas Cretaceous deposits overlap the Precambrian at the Hill Annex mine. More age determinations on the glauconites of the western Mesabi are needed to substantiate or refute this date. Several possibilities may be cited to explain the experimental finding. (1) Incorporation of older impurities. The sample analyzed by Hurley et al. was an unpurified rock chip and may have contained some detrital K-bearing minerals in addition to the glauconite. A small contamination by Precambrian K-bearing minerals would suffice to change the date from Cretaceous to Jurassic. (2) The Jurassic sea may actually have transgressed over this area without leaving any permanent fossiliferous deposits. (3) The glauconite may have formed during Jurassic time in marginal marine basins.

Glauconite has never been verified from Precambrian rocks. Schaub (29) has reported the occurrence of glauconite in Precambrian sediments on Ella Island, northeast Greenland, but Cloud (9) suggests that these sediments may be of Cambrian age. Opinion in the literature appears divided as to whether the lack of Precambrian glauconite is a consequence of unfavorable environmental factors or of the extensive recrystallization suffered by most Precambrian sediments.

Glauconite is generally interpreted as a product of diagenesis forming on the ocean floor from (1) alteration of biotite or other iron-rich minerals, (2) conversion of fecal pellets, (3) agglomeration of clay pellets, (4) foraminiferal cavity fillings, or (5) hydration of silica and subsequent absorption of bases. Takahashi (32) considers the latter as the essential process and the preceding four as possible sources for the hydrated silica gel. Burst (6)

summarizes the necessary physical-chemical requirements for glauconite formation as (1) the presence of the layered silicate structure, (2) plentiful supplies of iron and potassium, and (3) a favorable environmental oxidation potential. These requirements are perhaps most readily fulfilled in the marine environment, but this does not preclude the formation of glauconite under other specialized conditions, as is indicated by Keller (21).

The very interesting question can now be raised as to why glauconite did not form as a product of diagenesis at the time the Biwabic formation was deposited, rather than secondarily from the same materials at a much later date. Both physical factors within the basin of accumulation and the physical-chemical environment must be considered. Sedimentation of detrital material appears to have been slow, a factor favorable for glauconite accumulation. Little is known as to other factors, such as depth of water, temperature, turbulence, or currents, in the basin of accumulation but Cloud (8) has summarized evidence showing that an appreciable range in these factors is tolerated by Recent glauconites. If it is assumed that these factors are not critical, the answer would appear to lie in the physical-chemical environment. We do not have independent evidence, however, to suggest that one of the factors listed may not have been critical for the Biwabic basin.

Salinity may be a critical factor. Most investigators consider normal marine salinity as essential for glauconite formation, although Keller (21) has reported Al-rich material approaching glauconite in composition from the non-marine Morrison formation. Takahashi (32) cites Recent glauconite occurrences in marine bays and its absence in adjacent fresh-water bays along the Japanese coast, as well as Yagi's experiments on differential base uptake by colloidal silica in saline and fresh-water environments, to emphasize the importance of salinity. The salinity of the waters in which the Biwabic iron-formation was deposited is not known. Tyler and Twenhofel (33) concluded in the case of the similar Huronian iron-formations of Upper Michigan that the conditions were essentially fresh-water because of the low level of Ca and Mg in the iron formation and its gradational association with deltaic deposits. James (19), on the other hand, calls upon restricted basins connected with the open sea. Until more definite information is available, lack of the proper salinity level must be considered a possible reason for the absence of primary glauconite in the Biwabic. Other possibilities may be sought in the physical-chemical requirements given by Burst (6).

Of the three requirements listed by Burst the first two seem to be satisfied in the Precambrian iron-formations of the Lake Superior district. The writers are not aware of any studies that have been made to determine the presence of detrital, degraded micas in Precambrian rocks of this region. Greenalite, chamosite (7 Å type), 1 M muscovite, and chlorite are layer silicates, however, and can be found locally in abundance in unoxidized iron-formation. All available evidence indicates these to be primary silicates or, at least, diagenetic modifications of primary minerals. Chamosite, rarely, and 1 M muscovite and chlorite, commonly, can be found also as secondary minerals clearly associated with ore bodies (1). The two types of occurrences are sufficiently distinctive, however, that they need not be confused. Further

proof of the primary genesis of some 1 M muscovite is given by K-Ar age determination. Pyroclastic fragments in unmetamorphosed Gunflint iron-formation near Port Arthur, Ontario, have been altered diagenetically to greenish 1 M muscovite. Hurley et al. (18, p. 122) have reported a K-Ar age determination of 1600 million years for this material.

The requirement of an abundance of iron and potassium is also satisfied, at least locally. Iron is ubiquitous in the entire Lake Superior district. Potassium is present in stilpnomelane throughout the district and in the Gunflint 1 M muscovites. Conway (10) lists geochemical data to indicate that on a world-wide basis potassium was being incorporated in considerable amount in sedimentary rocks, presumably in authigenic micaceous minerals, reaching a peak in the late Precambrian and Cambrian. Nanz (25), on the basis of 36 analyses of fine-grained Precambrian rocks from the Lake Superior region, interprets his data as showing that potassium is equally abundant in lutites of all ages, including the Precambrian.

It has been shown that the chemical elements required for glauconite were available in Precambrian time as well as in later geologic eras. Also the primary iron-rich layer silicates, greenalite, chamosite, and 1 M muscovite, were able to form in the sedimentary and environmental framework represented in the Precambrian basins of accumulation. The absence of primary glauconite in the Biwabic iron-formation, therefore, seems to be related either to salinity level or to absence of a favorable environmental oxidation potential. Glauconite is essentially the iron-rich analogue of 1 M muscovite. As such, it requires a plentiful supply of Fe^{+3} ions to build its structure. The primary iron-rich silicates, greenalite and chamosite, found in the Minnesota and Michigan Precambrian iron-formations are dominantly ferrous, rather than ferric, varieties. They are based on the trioctahedral serpentine structure and have Fe_2O_3 : FeO ratios of 1 : 4 or less (4, 5, 16). Siderite, the other primary iron mineral found in the iron-formation, is also ferrous. Although the Gunflint 1 M muscovites do vary in color from white to dark green, perhaps due to variable total and ferric iron contents, partial analysis of the most iron-rich material (5.38 percent total Fe) shows a Fe_2O_3/FeO ratio of only 2.75/4.45 = 0.62 (Table 1). These figures are in contrast to the 16 to 25 per cent total Fe contents and Fe_2O_3/FeO ratios between 2.3 and 5.2 found for the glauconites of this paper. Whether the environmental oxidation potential responsible for lack of ferric ions is primarily the result of the nature of the atmosphere, the nature or abundance of life, the E_h of the waters, or some other interrelated phenomena remains a matter of conjecture.

The situation in the Biwabic iron-formation can not be extrapolated to a world-wide basis without better justification than now exists. Evidence is accumulating that primitive forms of life were abundant in the later Precambrian and that the atmosphere was not radically different from that of to-day (15, 19, 25, 26, 27). For these reasons the writers are not yet convinced that Precambrian glauconites are nonexistent. The present study does suggest that age determinations will be required for proof of the glauconite age, even though the host rock may be unquestionably Precambrian.

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SOURCE OF BRACKISH GROUND WATER IN PLEISTOCENE FORMATIONS BENEATH THE DUTCH POLDERLAND[1]

A. VOLKER

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FOREWORD BY J. E. UPSON[2]

THE paper that follows was originally presented by Mr. Volker in 1950 before a meeting of the Royal Netherlands Geological and Mining Society. It was never published. In the academic year 1958–59 the translator was in Holland under a Rockefeller Public Service Award studying the occurrence and origin of salty ground water, as well as Dutch methods of managing fresh ground-water resources in the coastal region. At that time the author very kindly made the manuscript, which was written in Dutch, available for study. In the course of that study, this contributor translated the paper into English because he felt that it represented a significant contribution to understanding of some aspects of sea-water encroachment.

Ordinarily one thinks of the salt water-fresh water contact in coastal ground waters as a comparatively sharp boundary. Indeed, it has often been considered as a sharp boundary for purposes of mathematical treatments. Also hydrologists generally expect that when a well penetrates the edge of a fresh-water body along a coast, such a well would enter salt water of near sea-water salinity within a depth of a few meters. With increasing knowledge, we are finding that this concept is incorrect for many areas, of which a large part of the Netherlands is one. There, salt water of variable, but generally low or moderate, salinity occurs beneath a thin body of fresh water. Beyond a certain depth, the salinity of the deeper water, as explored at several places, gradually increases over depths of several hundred meters. The main thesis of the paper is that the observed depth curve of chloride concentration can be explained in large part by modification of deep-lying older sea water and overlying fresh water through molecular diffusion operating over the long time interval since the early Pleistocene.

The author recognizes that diffusion is not the only mechanism operating; and there is room for disagreement in the specific correlation between the

[1] English translation by J. E. Upson.
[2] Research Geologist, U. S. Geological Survey, Mineola, N. Y.

computed depth-salinity curves and observed values, especially at shallow depths. However, the translator believes that these elements do not detract from the value of the basic contention, and that this application of the concepts of geologic history is an important contribution to our thinking about problems of sea-water encroachment.

The author, an accomplished linguist as well as hydrologist, would be quite capable of making the English translation of his paper himself. He has kindly approved and consented to the publication of the article in this version. The translator is pleased to be able to make this paper readily available to American hydrologists.

INTRODUCTION

The presence of brackish ground water in the Pleistocene formations is of large practical significance in connection with such problems as upward migration of salt water into polders, development of drinking water supplies, and water management. It is one of the pertinent factors to be considered in the Zuiderzee project (Fig. 1).

Figure 2 gives the change in chloride concentrations with depth in four borings in the IJsselmeer basin. In this basin apparently everywhere the chloride concentration increases with depth.

This paper discusses the origin of this brackish water. In looking for a quantitative explanation, little attention has been paid so far to the influence of diffusion. Diffusion is the movement of salt ions in quiet water under the influence of concentration differences; it can be described mathematically. It is believed that diffusion can furnish an appropriate explanation for the sequence of chloride concentration in the ground water beneath the IJsselmeer basin. For other areas, with a different sequence, a similar but different explanation might be possible.

EXPLANATORY HYPOTHESES

Table 1 gives a summary of the various explanations appearing in the literature pertaining to the origin of the salt content in the deeper strata (50–300 m below N.A.P.[3]). Between about 50 m and about 20 m below N.A.P. the chloride concentration decreases upward (Fig. 2), but increases again above the − 20 m level. Thus there is a shallow zone with "fresh" water. Various authors have presented different explanations for the origin of this "fresh" zone. These hypotheses are presented in Table 1.

An examination of the table shows that all the suggested theories are of a purely qualitative nature. Nowhere is there an effort to express in figures the influences of various factors such as displacement, intrusion, dilution with fresh water, mixing, or diffusion. Rather, the deeper salt is ascribed to circumstances arising from some episode of marine transgression within the geologic history (Fig. 4). The starting point for these ideas is that salt water above fresh water constitutes an unstable condition. A small disturbance will cause the salt water to fall with relatively great speed through the water-bearing layer to the bottom ("salt-water hypophyses of van der

[3] N.A.P., Nieuw Amsterdam Peil, is approximately mean sea level. [Translator's note.]

Hoeven"). The intruding salt water will then be distributed laterally by circulation currents especially in the deeper layers, and otherwise displace the fresh water from underneath.

There are several objections to this suggestion. One of them is that the observed distribution of salt does not fit the pattern that would be expected from this postulated downward and then outward flow of salt water

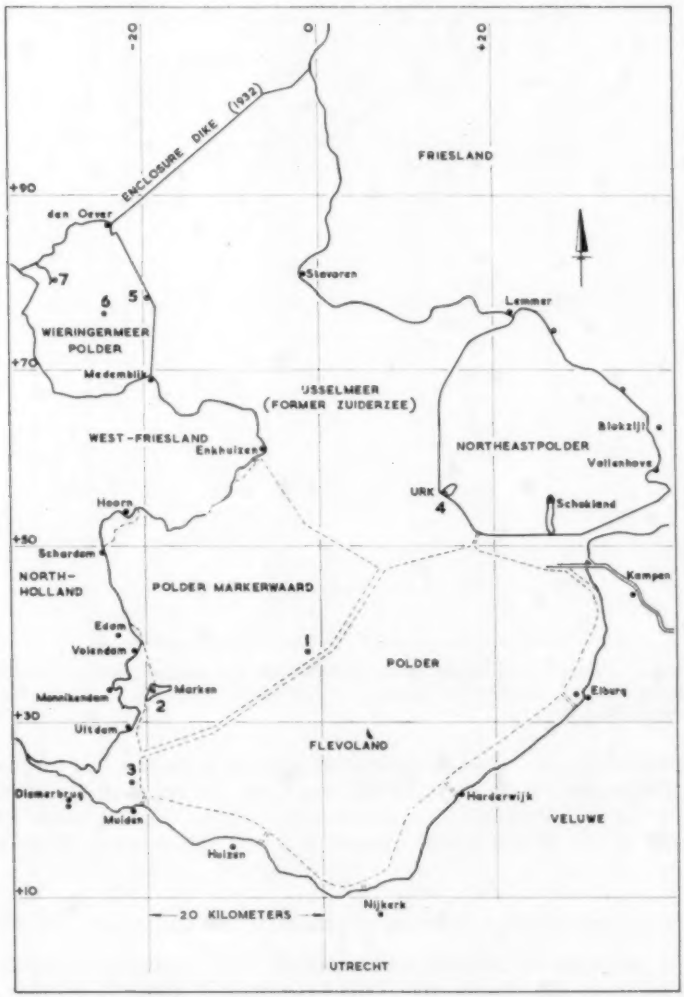

FIG. 1. Outline map of the IJsselmeer, the Netherlands, showing location of borings.

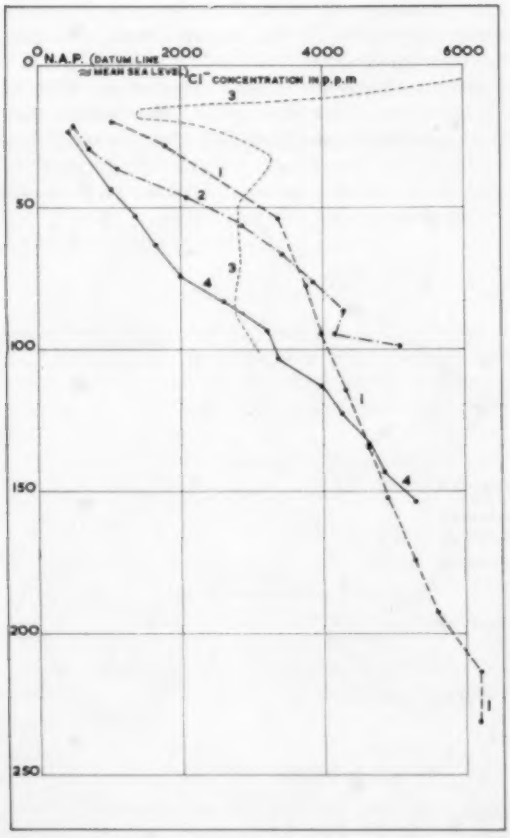

FIG. 2. Observed chloride concentrations of the ground water beneath the IJsselmeer basin. Depths in meters. 1, in basin (see Fig. 1); 2, Marken; 3, Pampus; 4, Urk.

in the deeper layers. Of even greater significance is the fact that the Zuiderzee transgression, in the early Middle Ages, has not resulted in such a pattern of salt distribution. This conclusion is drawn from a study of the sequence of salt content in the uppermost layers (above about 20 m below N.A.P.).

EXPLANATION OF SALT CONTENT IN THE SHALLOW LAYERS BY DIFFUSION

The sequence of chloride concentrations with depth was explored in some hundreds of borings in the IJssel Lake basin to about 15 m below lake bottom. Everywhere the sequence corresponds to the four types reproduced

TABLE 1

HYPOTHESES TO EXPLAIN THE SALT CONTENT OF GROUND WATER IN THE IJSSELMEER AREA

Author	Ref.	Date	Area investigated	Shallow "fresh" water 20–50 m below N.A.P.		Deep "salt" water 50–300 m below N.A.P.	
				Period of origin	Mechanism	Period of origin	Mechanism
Dubois Wintgens	1 2	1903 1911	Polders (!) Northholland	Historic time	Infiltration of fresh rain water	— —	— —
van Waterschoot van der Gracht		1910	Dune area	—	—	Zechstein (Upper Permian)	Upwelling of salt water from Ca and Mg rich pressure horsts from the Zechstein salt
Versluys	3	1917	Urk	Pre-Rissian fluvial Pleistocene	By ground-water flow in the Pleistocene from east to west, protected from salting from recent Zuiderzee by boulder clay. (Before this Urk was never covered by sea.)	Recent Zuiderzee (1200–1934)	Infiltration of salt water from recent Zuiderzee at places distant from Urk, where boulder clay is absent
Rijksbureau voor Drinkwater-voorziening	3	1918	Marken (prognosis)	Expectation was that fresh water also would be found at greater depth. Source: Veluwe, Gooi, or dunes during part of Pleistocene and Holocene, protected against Eem sea and later marine transgressions by: 1. Middle, fine, part of the diluvium. 2. Alluvial peat and clay layers.			
Versluys	3	1918	Zuiderzee and West-Friesland	Terrestrial period Young-Holocene (mainly I 5 v)	—	Old Holocene sea and Sea of Lorié	Infiltration of salt water by density difference (see below)
Versluys	3	1919	Marken	Part of Pleistocene and Holocene	From dunes of the Veluwe; flowed in as fresh water apophyses (allochthonous origin)	Old Holocene sea and Sea of Lorié	Infiltration of salt water by density difference. (Salt from Eem sea disappeared during Laagterras time by overpressure; as did part of the Tertiary salt during the pre-glacial diluvium.)
Rijksinstituut voor Drinkwater-voorziening—Zuiderzeewerken	4	1936	Wieringermeer	Young Pleistocene and old Holocene (I.O.v.)	Return encroachment of part of the salt from Eem time	Eem transgression	Driving out of whole fresh-water complex in Pleistocene time
van der Hoeven	5	1937	Northeast Polder southeastern part of the IJsselmeer basin	—	—	Zechstein (Permian)	Upwelling of salt water from water-bearing porous rocks under Tertiary beds. Salt rises to higher levels from salt beds of Zechstein time through faults.
Rijksinstituut voor Drinkwater-voorziening	3	1938	Northeast Polder	—	Fresh zone here actually present	Recent Zuiderzee (1200–1939)	Rapid infiltration of salt water by density difference, lateral movement of salt in deeper layers by circulating flow
Rijksinstituut voor Drinkwater-voorziening	3	1939	Basin of the IJsselmeer	Young Pleistocene (under boulder loam (till of Riss age), itself old Pleistocene)	In spite of coarse beds, freshening in this period much less than in Wieringermeer	Eem transgression	Recent Zuiderzee transgression is still not in important measure intruded because of protective covering of layers of Holocene age. Because of absence of typical deposits of the Old Holocene and Old-Young Holocene sea, salting is hereby less probable.

in Figure 3. It appears now that these chloride concentrations can be explained entirely by diffusion.

The freshening in the uppermost few meters results from the fresh IJsselmeer water replacing the brackish Zuiderzee water after the closing of the Afsluitdijk in 1932 (Enclosure dike, Figure 1). This freshening still continues; and from borings made in the IJsselmeer bottom in 1936, 1938, 1942 and 1947, it appears to have proceeded as would be expected from

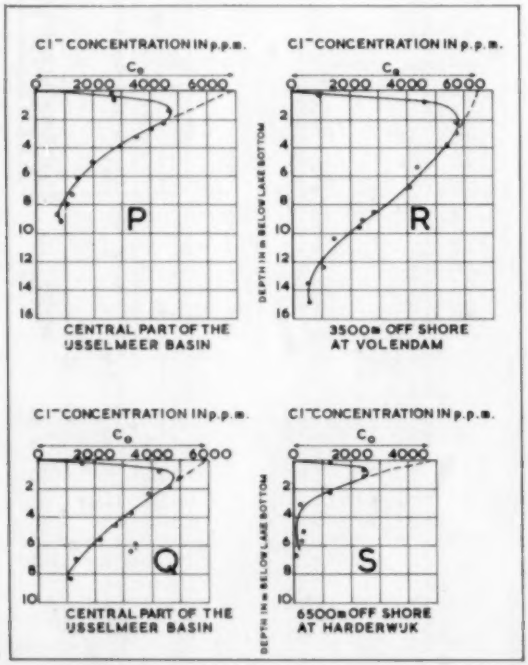

FIG. 3. Observed sequence of chloride concentration in the upper few meters beneath the IJsselmeer basin. o, observation; C_0, chloride concentration of water in former Zuiderzee.

laboratory tests and mathematical theory. Further investigation showed that the sequence to a depth of 15 m can also be explained by diffusion.

Since the early Middle Ages (about 1325 A.D.) salt from the recent Zuiderzee has invaded the fresh ground water that was formed during the previous long terrestrial period. Diffusion proceeds so slowly that since the formation of the Zuiderzee, not enough time has passed for the ground water to be entirely salted. Yet nowhere is evidence found for a downward moving salt flow, such as, according to the circulation theory, ought to occur at different places. The net of borings is so thick that, if such flows were

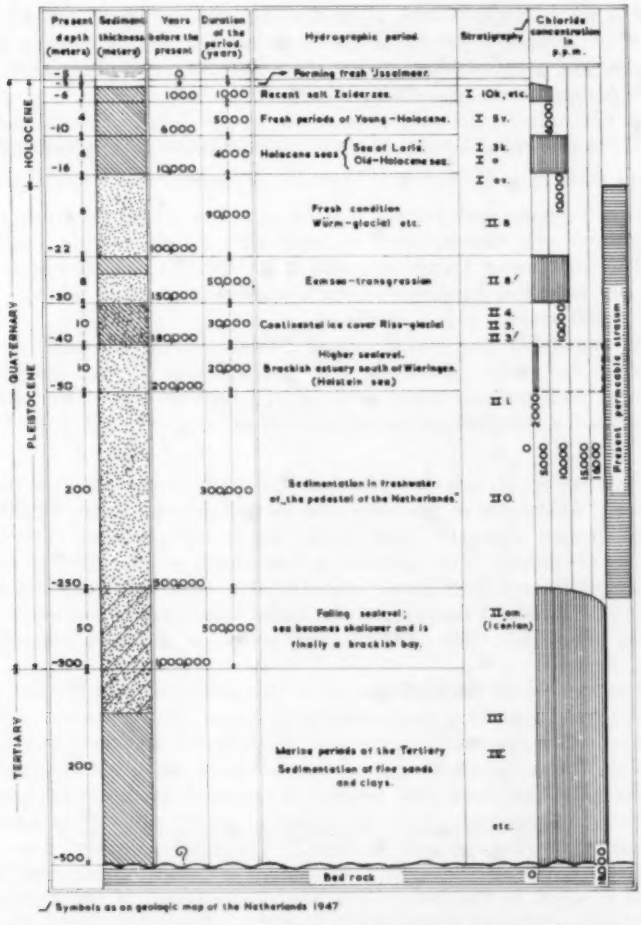

FIG. 4. Diagram showing stratigraphy beneath the IJsselmeer basin, estimated duration of episodes in years, and estimated chloride concentration of water initially present.

present, it may be considered out of the question that they would be missed.

The salt content in the surficial layers (uppermost 20 m) can thus be explained quantitatively.

The fact that the influence of the last marine transgression and a subsequent fresh period can be reconciled with the theory of diffusion leads one to look into whether or not the salt content in the deeper layers can be explained in the same way.

Toward that end it is necessary to recognize the different fresh and salt

periods of the geologic history, their duration, the sediments formed therein and the salt concentration during the periods. For the IJsselmeer basin, at a place 40 km north of Amersfoort, these data were supplied by dr. ir. P. Tesch. A diagram is reproduced in Figure 4.[4]

DIFFUSION OF THE SALT OF THE OLDER MARINE TRANSGRESSIONS

Three main periods, shown in Figure 4, apparently apply to this problem:

a. The Tertiary and Icenian during which a great thickness of fine-grained beds was deposited in water with a high chloride content.
b. The pre-Rissian Pleistocene with a 200-m thick, mostly coarse, sandy layer deposited by floods of fresh river water over a period of about 300,000 years. (II, 0 in Fig. 4.)
c. A comparably long period (about 200,000 years) with much less sediment formation (about 50 m), characterized by an alternation of fresh and brackish water periods, in which the IJsselmeer area constituted a marginal sea, a sea arm, or an estuary. (II, 1 to I 10k in Fig. 4.)

For spreading of salt by diffusion, the main period (a) is the most important. At the end of this very long marine period (about 500,000 years ago) the ground water to great depths had a high chloride concentration (about 18,000 ppm). The question is, how much of this salt has remained and how has it been distributed, and what has been removed? It appears that this is determined entirely by the hydrologic situation during the sedimentation of II 0. (The 300,000-year period of fluviatile deposition in pre-Riss time.)

One must imagine the Netherlands in this period as a rather flat terrane having a gentle slope in a northwesterly direction, with a scanty vegetation, throughout which continuously repeated river floods deposited great quantities of sand. If any ground-water movement has occurred, such ground-water movement must have been slow because of the small gradient and because of the fact that a large part of the precipitation would run off, in contrast to the situation in the present Veluwe.[5] This ground-water flow—which according to van Waterschoot van der Gracht is named "continental flow"—extended in depth to the fine-grained and clayey layers of the Tertiary and Icenian (presently about 250 m below N.A.P.). Below this level, freshening extended further by diffusion.

Figure 5 suggests, for two different sets of assumptions, what has become of the salt from the Tertiary and Icenian in the 500,000 years since the beginning of the fluviatile Pleistocene.

In the first set of assumptions, the continental flow during the 300,000 years of sedimentation of the II 0 is assumed to have been so strong that

[4] Naturally, information, new in several respects, has appeared since 1939. For the following discussion this is of little importance.

[5] The Veluwe is a region in central Netherlands composed of glacial deposits mainly of sand and gravel. It consists of irregular hills in which the land surface is underlain by very absorptive material, and from which there is virtually no direct runoff from rainfall. [Translator's note.]

during this period the ground water was entirely fresh to the base of the fluviatile deposits. Curve A in Figure 5 shows the salt content of the Tertiary and Icenian after these 300,000 years. The sedimentation had then progressed to the level now about 50 m below N.A.P. In the succeeding 200,000 years this salt has moved up by diffusion. This distribution (of salt) is also given in Figure 5 (Curve B). We will return to a discussion of the influence of sea and land stages in this period.

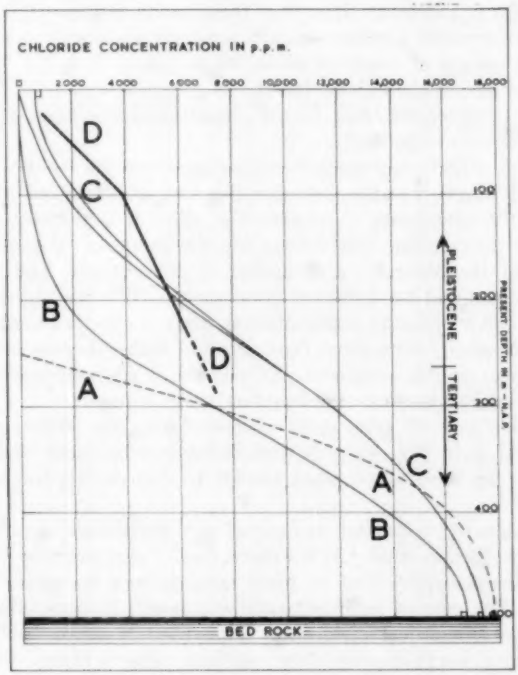

FIG. 5. Calculation of diffusion of salt from the Tertiary and Icenian deposits beneath the IJsselmeer basin. A, influence of the complete desalinization of the II 0 during 300,000 years; B, diffusion during 200,000 years; C, diffusion during 500,000 years; D, observed sequence of chloride concentration in the IJsselmeer basin.

Next, the probable distribution of the salt content is calculated for the second set of assumptions under which the "continental flow" was too weak to keep the water in the Pleistocene deposits entirely fresh. In that case, the salt from the Tertiary and Icenian would have been able to move upwards throughout the entire 500,000 years. Curve C in Figure 5 shows the distribution that thereby would result. It is to be expected that, especially in the layers deeper than 200 m below N.A.P., actually lower chloride concen-

trations would appear. (The slightly divergent upper parts of Curve C represent the use of different limiting values.)

With respect to the fresh and brackish stages of period (c), calculations show that the period of terrestrial conditions that has followed each marine transgression has in large part removed the salt that diffused into the ground. However, there still remained, after the Würm glacial period and after the fresh period of the Younger Holocene, 12½ and 15 percent, respectively, of the salt that had invaded the soil by diffusion during the preceding sea invasion. Rough calculations show that these modifications—ignoring the salt from the Tertiary and Icenian—would produce a chloride concentration of 2000 to 2500 ppm at a depth of about 80 m below N.A.P. This influence did not extend deeper than about 160 m.

The last transgression, that of the recent Zuiderzee, has no significance in the origin of the deeper salt.

In Figure 5, where only the salt originating from the Icenian and Tertiary is represented, Curve D also indicates the average observed distribution in the basin of the IJsselmeer (compare Fig. 2). If one compares this with the calculated distribution, and allows for the influence of period (c), then it appears that the observed distribution, if not entirely, still for the most part, can be explained by diffusion phenomena. The mainly three-cornered distribution of the chloride concentration finds a ready explanation in the foregoing discussion. One must bear in mind that, whereas other "disturbing" factors also doubtless appear, diffusion is a phenomenon that operates under all circumstances, and certainly has some influence.

The question can still arise as to whether during the Würm glacial period (Laagterras, II 8 in Fig. 4) a partial flushing to a depth of about 250 m below N.A.P. can have taken place similar to that during the sedimentation of II 0.

One can develop a partial picture of the hydrologic conditions during the younger Laagterras time. It is known that at that time the Dutch terrane displayed a distinct relief that in many aspects was comparable to that of the present. The rate of sedimentation was small, in comparison with that during the older fluviatile Pleistocene. Thus the terrane probably was not so much an evenly north-sloping delta surface, where rivers by continuous flooding could deposit their load over large areas in thick beds.

For the existence of a continental flow—which is not out of the question for II 0—there are no obvious reasons. Just as under present conditions, the occurrence of a ground-water flow was entirely dependent on the local situation, in spite of the general slope in a northerly direction.

In addition, the duration of Laagterras time was much shorter than of II 0. A significant general flushing of the Pleistocene deposits in the whole IJsselmeer area therefore seems to be out of the question.

EXPLANATION OF SALT CONTENT IN OTHER AREAS

The foregoing mainly has reference to the salt content beneath the IJsselmeer basin. Obviously, other places with a different salt content

should be tested for quantitative explanations based on the diffusion principle. A systematic investigation to compare the salt content of the deeper ground water in different parts of the Netherlands, however, has not yet been carried out, so that only a few disconnected comments follow below.

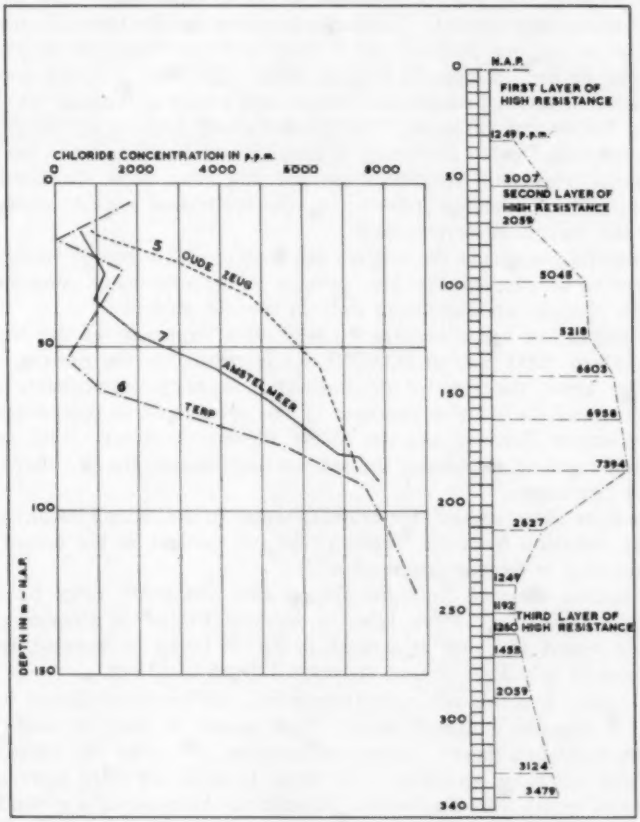

FIG. 6. Observed chloride concentrations: left, beneath the Wieringermeer shortly after reclamation; right, in the deep boring at Diemerbrug.

The northwestern part of the land always has lain the farthest seaward from the coast line of the former seas, so that in general the marine periods have lasted longer there than elsewhere. Also, in the north the salt content of the sea water was the highest (cf. the recent Zuiderzee). Possibly the freshening of the Tertiary layers during sedimentation of II 0 would have been of less significance here than elsewhere; the continental flow had already

travelled a long way over the salt Tertiary. Finally, the presence of the Holstein sea (II 1) must be taken into account.

If one introduces these factors into the calculations, then it seems possible to explain the sequence of salt content, as it has been observed beneath the Wieringermeer (Fig. 6; for location see Fig. 1).

The influence on the salt contents of the ground-water flow especially must be taken into account. Ground-water flow results from the formation of infiltration regions such as the Veluwe and the Gooi,[6] or is artificially maintained by the drainage of deep polders. The very low salt content in the Pleistocene strata beneath the Veluwe is a result of flushing for 180,000 years by infiltrating rainwater. At greater depth (350 m at Harderwijk), where the ground-water movement is insignificant because of the fineness of the material, there still remains some salt that came from the Tertiary by diffusion. The freshening influence of the infiltration regions extends out only to the immediate surroundings.

In polders, changes in the original salt content of the ground water appear very slowly, because of the low velocity of ground-water movement, so that these changes are significant only in the old polders.

The rather low salt concentration beneath a large part of the Northeast Polder (about 3000 ppm at 200–250 m) is related to the presence of the infiltration areas, the zone of ground-water discharge immediately east of the polder, and the relative nearness of the coast lines in successive stages of the youngest Tertiary and the oldest Pleistocene times. This last fact is also important in explaining the salt content beneath the provinces Friesland and Groningen.[7]

In case, as above argued, the brackish water in the older Pleistocene originated by diffusion from the Tertiary, the salt content in the deeper strata should increase in regular progression.

Information obtained from the Diemerbrug test hole[8] (Fig. 6) is contradictory to this idea. Here, below a depth of 185 m the chloride concentration decreased, and then at a depth of 250 m began to increase, reaching a maximum of only 3500 ppm at the bottom depth of 335 m.

It is certain that this salt came from below, yet for the shallower brackish water this apparently doesn't hold. This boring is thus in conflict with the above-developed theory, unless one assumes that after the formation of the Utrecht hill ridge (moraine) the strata beneath the third layer of high resistance (Fig. 6) were flushed out through the influence of a ground-water flow which beneath this bed could extend as far as in the younger Pleistocene.

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May 12, 1961

[6] The Gooi, a short distance east of Amsterdam, is a sandy, hilly region similar to the Veluwe. [Translator's note.]

[7] The two northeastern provinces of the Netherlands. [Translator's note.]

[8] According to Faber (6) the top of the Icenian here lies at 191 m and the top of the Amstelian at 244 m.

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STUDIES ON THE OXIDATION OF GOETHITE

K. V. G. K. GOKHALE

ABSTRACT

Goethite on heating in air, undergoes both oxidation and dehydration. X-ray investigations of the heat-treated samples of goethite at different temperatures indicate hydrogoethite, maghemite (hydro?) and hydrohematite as intermediate products prior to the conversion into hematite. This paper summarizes the various possible stages of transformation, on heating in air, of goethite due to oxidatior and dehydration, and a correlation has been made with the differential thermal studies of goethite.

In an earlier paper (1), the author has presented the studies of oxidation stages of magnetite, in which it is indicated that magnetite is susceptible to oxidation even at moderate temperatures. In the present paper a further attempt is made to study the oxidation states of hydrated iron oxide i.e. goethite at moderate temperatures. A theoretical discussion on the possible oxidation states is followed by the experimental work and its interpretation in the light of the present-day status of this subject.

THEORETICAL DISCUSSION

The D.T.A. curves of goethite indicate a prominent endothermic peak round about 360° C and show no further susceptible changes. Since in D.T.A., the sample is heated at a quicker rate through a wide range of temperature, it is not possible to identify the different states of oxidation during such thermal analyses. The endothermic peak is observed for 15 minutes time range and it is sharper at 360° C (when the rate of heating is 10° C per minute); hence it was thought logical to heat the samples of goethite in air at that temperature range for varied time from 5 to 15 minutes. These samples have been x-rayed to distinguish the changes in crystalline structure. Further heating at about 600° and 950° C for a fairly long time has been done to study the subsequent changes in oxidation states.

The heating of goethite involves two changes, namely, dehydration and oxidation. The possible changes are dependent on the extent of dehydration and oxidation. The relation between goethite, magnetite and hematite during process of heating can broadly be indicated as shown in Figure 1.

Goethite on very short heatings shows a tendency to convert to hydrogoethite by partial expulsion of combined water; on further heating it may give rise to several partially hydrated iron-oxide minerals. If the conditions favor, goethite may be transformed to hydromagnetite by controlled oxidation with concomitant dehydration. On heating in air, goethite does not transform to pure hydromagnetite, and forms a mixture of hydromaghemite with

hydrohematite. Prolonged heating will ultimately transform it to hematite. This is a case of solid/gas type of reaction, wherein two processes, i.e. oxidation and dehydration take place simultaneously. In nature, apart from the changes discussed above, goethite may also undergo still further changes in structure due to varied conditions of oxidation and dehydration.

It may be mentioned here that the author's theoretical studies cited earlier are in conformity with Nambu's (3) field studies.

EXPERIMENTAL STUDY AND RESULTS

Differential thermal analyses of representative samples of goethite were made and in all cases there is a conspicuously sharp endothermic peak during 350–360° C. The peak is visible for about 15 minutes. To have a clear idea about the changes that take place during the endothermic reaction, as also about the structure of the intermediate products during that period, samples were prepared by heating goethite for 5, 10 and 15 minutes respectively during the peak range and by suddenly quenching them to room condi-

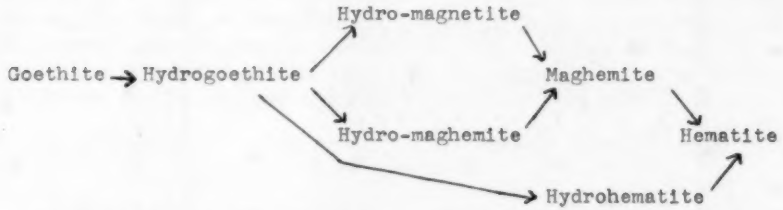

FIG. 1. Schematic diagram showing possible changes during oxidation and dehydration of goethite.

tions. The X-ray powder patterns have been obtained by using cobalt radiation. Samples of goethite have also been heat-treated at 600° C and 950° C respectively for 3 hours and analyzed by X-ray diffraction patterns.

The d-values of the different lines of the individual samples at those temperature ranges are summarized in Table I.

The diffraction lines of sample K/I can be correlated to the values obtained for standard goethite. Some extra lines indicate impurity. The lines shown by sample K/II contain, besides the lines of goethite, additional strong lines namely 4.18, 2.660, 2.467, 2.174, 1.553, 1.500 and 1.455. These lines correspond closely to the values given for hydrogoethite (2). Sample K/III also shows lines of goethite and those of hydrogoethite.

Sample K/IV is of goethite heat treated for 15 minutes at 350° C and contains lines corresponding to those of magnetite. These appear to be due to maghemite (hydro?).

Samples K/V contains lines almost similar to hematite but differing from it slightly. In consideration of the conditions under which it is produced, and in view of its similarity to hematite, it would be more justifiable to

Table I

X-ray powder patterns of goethite at different temperatures

K/I		K/II		K/III		K/IV		K/V		K/VI	
d(A°)	I	d(A°)	I	d(A°)	I	d(A°)	I	d(A°)	I	d(A°)	I
3.850	S	4.700	W	4.830	W	4.100	M	4.970	W	4.04	VW
2.750	VS	4.180	VS	4.430	W	3.675	W	4.200	S	3.66	W
2.560	S	3.385	W	4.175	VS	2.670	S	3.350	W	2.70	S
2.247	W	2.660	S	3.385	M	2.495	S	2.670	S	2.52	S
1.864	W	2.467	S	2.660	S	2.196	S	2.464	S	2.440	W
1.712	VS	2.174	S	2.467	S	1.835	W	2.229	W	2.190	S
1.600	W	1.710	S	2.171	S	1.696	VS	2.182	S	2.020	W
1.520	S	1.684	VW	1.685	VW	1.570	W	2.090	VW	1.835	S
1.464	S	1.553	M	1.657	VW	1.480	W	1.919	VW	1.685	S
1.320	W	1.500	M	1.596	W	1.452	S	1.790	VW	1.580	M
1.262	VW	1.455	M	1.558	M	1.358	W	1.716	S	1.485	S
1.147	VW	1.386	M	1.501	M	1.312	W	1.686	S	1.440	S
1.115	M	1.356	M	1.458	S	1.260	W	1.651	W	1.306	M
1.060	W			1.394	VW			1.601	W	1.255	W
				1.363	W			1.560	S		
				1.321	W			1.505	M		
				1.260	M			1.457	S		
				1.146	VW			1.396	M		
				1.125	VW			1.362	M		
				1.098	M			1.319	VF		

K/I Goethite.
K/II Goethite heated for 5 minutes at 320-350°C.
K/III Goethite heated for 10 minutes.
K/IV Goethite heated for 15 minutes.
K/V Goethite heated for 3 hours at 600°C.
K/VI Goethite heated for 3 hours at 950°C.

assume it to be hydrohematite rather than hematite itself. Sample K/VI has all the lines of hematite.

Thus the spacings of the different lines for hydrohematite and maghemite (hydro?) quite agree with the values cited by Nambu (3) and those for hydrogoethite with the values given by Mihaev (2).

CONCLUSIONS

From the above results, the process of changes in goethite may be concieved as follows:

Goethite first dehydrates itself and is transformed to hydrogoethite. On further heating, hydrogoethite undergoes both oxidation and dehydration simultaneously and the formation of maghemite (hydro?) and hydrohematite take place around the temperature ranges of 350–360° and 550–600° C respectively, and finally they are completely converted to hematite at 950° C. The conspicuous endothermic peak for goethite during DTA around 350° C is thus not only due to dehydration as explained by the earlier workers, but also appears to be the resultant of simultaneous oxidation and conversion of goethite to hydrogoethite to maghemite (hydro?). Though the precise temperature ranges of conversion of hydrogoethite to maghemite, and its subsequent transformation to hydrohematite, and in its turn finally to hematite cannot clearly be defined, the author visualizes the following process of changes due to oxidation and dehydration of goethite on heating:

$$\text{Goethite} \rightarrow \text{hydrogoethite} \rightarrow \text{maghemite (hydro?)} \rightarrow \text{hydrohematite} \rightarrow \text{hematite}$$

In view of the progressive oxidation and since maghemite is nothing but oxidized magnetite, it is more justifiable to assume maghemite (hydro?) instead of hydromagnetite as the next stage to hydrogoethite. The coexistence of these minerals in nature has been reported by Nambu (3).

Thus it appears that the structural changes, involved in dehydration concomitant with oxidation, need detailed study. However, the experimental results cited now, appear to justify the author's theoretical interpretations, on the nature of possible intermediate stages during oxidation along with dehydration of goethite. There appears to be a number of ways in which dehydration of goethite can take place in oxidized conditions. Further studies alone will give us a good basis for the identification of these stages.

In order to apply the experimental data for natural iron oxide mineral assemblages, the studies made so far are not quite conclusive. But it is certain, that in nature too, there exists a coexistence of such mineral assemblages as has been reported by Nambu (3). Further work to elucidate and clarify the phase relationship of this system is in progress.

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ORGANIC SEQUESTRATION OF COPPER

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ABSTRACT

A swamp in southeastern New Brunswick contains up to ten percent copper (dry weight) in forest peat. This mineralization is unusual in that the metal is not present in megascopic lumps of native copper but, rather, is invisible and appears to be in inorganic combination. Factors responsible for the movement of the metal in the mobile state are clearly diffusion, capillarity, evaporation, and the growth of frost crystals. The phenomena liable for the fixation of the copper are less apparent. Vegetal concentration, sorption, and coprecipitation have no doubt produced minor modifications of the dispersion pattern. The dominant factor effecting the immobilization of the metal, however, appears to be sequestration of the copper by the organic sediments, thereby forming a chelate compound. On the basis of this study, the only value that can be assigned to the activity of microbes is, possibly, a catalytic effect, speeding the formation of the copper compound already stable under the chemical conditions imposed by the environment.

INTRODUCTION

THE Tantramar swamp in southeastern New Brunswick contains anomalous quantities of copper in black forest peat. This swamp was described earlier (5). It embraces 2½ acres of which one acre is open and the remainder covered by a swampy forest. The dominant material of the clearing is a sandy loam containing less than one percent [1] organic matter. A bare peat bank sits on the sandy loam at the southern margin of the clearing and swampy forest; this peat assays 3 to 10 percent copper and 60 to 80 percent organic matter. The swampy forest to the south consists of a continuation of the

[1] Assays are referred to soil dry weight.

peat bank, and is covered by vegetation, mainly evergreens; the copper content diminishes southward. Two hundred feet south of the clearing, the swampy forest gives way to the alder swamp which has less than 0.1 percent copper in its muck. While the alder swamp is not considered a part of the Tantramar copper swamp for pedalogical reasons, it is of interest in that this is the only sector in which the oxidation potential lies on the negative side of zero; the Eh of the alder swamp muck averages − 0.1 volts compared to the + 0.2 volts of the forest peat.

The Tantramar copper swamp is unusual in that, rather than containing native copper in lumps and aggregates as appears to be the normal situation in other cupriferous bogs (cf. Cornwall, 3), the copper substance is invisible and could not be separated from the peat by either "gold" panning, heavy bromoform liquid settling, or by the utilization of an isodynamic separator. Consequently, the enigmatic copper substance does not appear to have a specific gravity nor a magnetic susceptibility characteristic of most metals or their derived oxides and sulfides.

The history of the area can be deduced from three basic facts: (a) the cupriferous solutions enter the copper swamp through water seepages that emerge in the clearing, (b) while the maximum copper content occurs on the surface of the bare peat bank, the high metal zones extend underground beneath the swampy forest (cf. Fig. 2, ref. 5), and (c) in the swampy forest, surface humus containing 0.3 to 1.0 percent copper supports the growth of a wide variety of plants (1), while at only four inches depth the peat appears having a copper content of 2 or 3 percent, which reaches a maximum of 5 percent at a depth of two and three feet.

From these three facts, the history of the area can be reconstructed as follows: The clearing, once covered by the swampy forest, is a response to copper toxicity. Above the seepages, the preexisting forest peat absorbed the highest amounts of copper, resulting in the death of the overlying flora. As a gradually widening area developed, rapid evaporation had the effect of raising the cupriferous solutions to the surface. This brought high concentrations of copper into contact with the feeder roots of plants, growing at the margin of the clearing, which had hitherto received a degree of protection from the few inches of low-metal humus. This resulted in the expansion of the clearing at the expense of the swampy forest. Rain, along with the waters from the seepages, has eroded the peat in the clearing, thus exposing the underlying sandy loam. An outflowing streamlet, fed by seepage water, is at present steadily eating away at the bare peat bank and is thereby slowly removing the cupriferous peat from the Tantramar copper swamp.

THE PROBLEM IN FOCUS

This paper attempts to elucidate the mechanism liable for the entrapment of the copper in the forest peat and, as this mechanism must be compatible with the observed field features, the above summation of an earlier paper (5) is essential if the reader is to judge the merits of the following argument. There are many factors that quite likely influenced the development of the

Tantramar dispersion pattern (as depicted in the cross-section of Fig. 2, ref. 5). This paper examines several of the most obvious of these factors and attempts to determine which one is the dominant. It is argued that the phenomenon of chelation is the most reasonable possibility of the several factors investigated in regard to the fixation of the copper. The formation of a chelate compound of copper is not unequivocally proven, but is suggested as a means of explaining the invisibility of the Tantramar copper and its close affiliation with the organic sediments. It is realized that finely divided native copper or cuprous oxide, the latter being compatible with the pH-Eh association in the peat, could hold the answer to this enigmatic copper substance. However, as no trace of inorganic copper minerals was discovered (apart from surficial films of malachite and, possibly, azurite), the chelation hypothesis was developed in detail. It will be shown that (a) each copper atom may be bonded to four nitrogen atoms in the peat when the metallic content is less than one percent, (b) between one and two percent copper, oxygen must increasingly substitute for nitrogen, thereby resulting in the metal atom being bonded to two nitrogen and two oxygen atoms, and (c) above two percent copper, four oxygen atoms must be bonded to part of the copper in the peat.

MOBILITY OF COPPER

The mobility of copper in the surficial environment, and the factors governing it, is of particular interest in the study of the possible processes involved in the mineralization of the Tantramar swamp. Mobility, or the ease and speed with which copper moves, may be the resultant of a vast complex of physical, chemical and biological factors. In the following discussion of the agents that may be responsible for the development of the Tantramar dispersion pattern, it is assumed that the most likely form of the metal in the mobile state is that of the divalent copper sulfate.

Physical Factors Affecting Mobility

The dispersion pattern depicts the distribution of the copper in relation to the focus of enrichment, and this in turn reflects both the abundance of copper in solution and the equilibria characteristic of the environment. The cupriferous solutions emerge as seepages in the clearing and are absorbed by the forest peat. The cross-section (5, Fig. 2) shows clearly that the apportionment of copper is dependent on the physical distribution of the forest peat, and that the "homogeneity" of the dispersion pattern is fairly high, i.e. few erratic values occur as the copper percentages decrease evenly in a direction away from the clearing. This homogeneity indicates the importance of diffusion, as it suggests that an equilibrium exists between the concentration of copper in the mobile and immobile phases.

The effect of capillarity can be seen on the peat bank in late autumn, when one day's growth of frost crystals will be pushed up by the crystals of ice forming the following day. Since the effect of capillarity is to collect and remove moisture by either evaporation or the feeding of growing frost crystals,

then copper ions should become enriched in the aqueous phase as the water is removed. The resulting dispersion pattern should then show a close correlation to the surface of the bare peat bank and, indeed, it does. However, in the swampy forest, the higher percentages are not found on the surface but, rather, at a depth of two or three feet, thereby reflecting the much lower soil irradiation. Hence, the role played by capillarity in the concentration of copper is only effective in the bare peat bank.

Vegetal Factors Affecting Mobility

Plants may play an important role in the overall movement of copper in the surficial environment. Their root systems can be portrayed as sampling mechanisms, bringing representative solutions up from a large volume of ground below the surface. Then, as the water is removed by evaporation, the mineral content of these solutions is left behind and thus concentrated in the vegetation (9). As the Tantramar copper is predominantly confined to the peat, it might seem reasonable to assume that the living plants have played a major role in the fixation of the metal.

Such a process could then account for the Tantramar dispersion pattern in the following way: vegetal action resulted in the concentration of copper by the assimilation of cupric sulfate solutions and, as the process continued, the toxic effect of the metal caused the death of the plants. New plants grew for a short while then also died.[2] With progressive burial and volume decrease due to decomposition and compaction, during which the peat was produced, the copper content would be further concentrated. Evidence supporting this hypothesis is found in the fact that the mosses most capable of forming peat (the so-called peat mosses, *Sphagnum* and *Hypnum*) are common in the swampy forest, and analyses of them by Beschel and Holman reveal that they can assimilate at least 50 ppm copper over soil containing 75 ppm. Other plants, such as the liverwort *Scapania*, contain 2,250 ppm when growing on peat assaying 4,300 ppm. The moss *Pohlia*, growing in the seepages of the clearing, assimilates up to 33,000 ppm (3.3 percent) over sandy loam containing less than one percent copper (Beschel, personal communication).

The vegetal assimilation hypothesis outlined above must be examined in the light of the probable history of the Tantramar swamp. In the *Introduction*, it was shown that the open area (clearing) probably resulted from the erosion of the swampy forest in conjunction with progressive copper poisoning of the flora. Therefore, conditions presently existing in the swampy forest must be compatible with the hypothesis if it is to be accepted. In this sector, plant growth is supported by a few inches of humus containing only 0.3 to 1.0 percent copper (1); at four inches of depth the peat appears and the copper content increases to 2 or 3 percent, reaching a maximum of 5 percent at a depth of two and three feet. It was assumed that the low evaporation

[2] That such a process is possible is implied in a statement by Beschel (1): "Seedlings of spruce, fir, and paper birch die with less than three inches height in the *Pohlia* mat." (This moss mat in places contains more than one percent copper.)

in the swampy forest prevented the bulk of the cupriferous solutions from reaching the humus, thus explaining the low metal concentration in the A_0 horizon.

The following evidence is considered not in harmony with the vegetal assimilation hypothesis: while the copper content of the peat beneath the swampy forest increases from 2 to 3 percent at a depth of four inches, to 5 percent at a depth of two and three feet, the consistency of the peat changes little over this range; this suggests that the organic accumulation has not been subjected to the compaction necessary to double the copper content. Further, it is doubtful whether the humus could undergo the size reduction required to produce the five- to one hundred-fold increase in copper needed to yield the percentages found in the immediately underlying peat. Hence, it is concluded that the assimilation of copper by plants, with subsequent concentration by vegetal decay and compaction, is capable of effecting only a minor modification of the Tantramar dispersion pattern. Rather than supporting the progressive downward enrichment demanded by the vegetal assimilation hypothesis, the copper distribution indicates that the immobilization of the metal has occurred during the migration of cupriferous solutions upward through the peat. The mechanism primarily responsible for the copper fixation must then be sought in the decayed organic matter (peat), not in the living plants.

Chemical Factors Affecting Mobility

The study of the Tantramar dispersion pattern is the study of the behavior of copper in aqueous solutions. The properties of ionic solutions which could be considered as contributary factors in the fixation of the metal in the forest peat are: solubility of salts, coprecipitation, adsorption and absorption, hydrogen-ion concentration and oxidation potential, and the formation of complex organic compounds. All of these factors undoubtedly have at least minor effects on the Tantramar dispersion pattern. However, the problem is to determine which factor is dominant.

Solubility of Salts.—The ability of a copper ion to remain in aqueous solution is limited by the solubility of the salts it forms with ions of opposite charge present in the same solution. The solubility product rule states that a copper salt may be precipitated from a saturated solution by increasing the concentration of any of the participating ions. In the Tantramar swamp, Beschel (1) noted that the surface of the bare peat bank, "becomes quite bluish after long dry spells (in summer) and the pH rises then to 8.1." During the autumn and spring when the writer visited the area, the pH was 7.2 or less and the blue color was not evident. Presumably the carbonate, azurite, was responsible for this unusual coloration and it is assumed that its precipitation was due to the insolubility of the carbonate ion in equilibrium with the copper at that elevated pH.

Thus, the solubility product rule, strictly in relation to the concentration of the copper cation and the participating anion(s), appears unable to account for the quantitative extraction of copper ions from solution. The carbonate

ion was shown to be ineffective in the formation of a stable copper compound, as rain tends to dissolve the bluish material. The sulfide ion undoubtedly plays a minor role as assays indicate that the peat contains only 0.2 percent sulfur (two independent sources [3]).

The importance of the oxygen anion in the mineralogy of the Tantramar copper cannot be established as easily as can that of the carbonate and sulfide ions. The presence of an oxide of copper in the peat was not disproved; this will be considered in more detail later.

Coprecipitation.—Hawkes (9) states that the precipitation of iron as limonite can carry down "substantial amounts" of copper. Experiments performed in an attempt to separate the Tantramar copper mineral, while being totally unsuccessful, resulted in observations that may be applicable to the evaluation of coprecipitation as a contributary factor in the production of the Tantramar dispersion pattern: (a) Peat containing 5.7 percent copper, taken from the surface of the bare peat bank and placed in bromoform (a liquid of specific gravity 2.89), resulted in the sinking of a few heavy particles. An X-ray of both heavy and light portions yielded the same unidentifiable pattern. (b) Peat having 5.1 percent copper, obtained from a depth of three feet in the swampy forest, did not sink at all in the heavy liquid; an X-ray of this material yielded the same pattern.

It is believed that these observations can be best explained on the assumption that the surface material had a higher content of iron (and perhaps manganese) in the form of limonitic (and pyrolusitic or manganitic) coating which resulted in a few of the peat crumbs sinking in the bromoform. As the iron-manganese content of the peat appears unrelated to the concentration of the copper, it is therefore concluded that coprecipitation is not primarily responsible for the immobilization and fixation of the Tantramar copper.

Adsorption and Absorption.—About 25 percent of the Tantramar peat is noncombustible, and this proportion appears to consist largely of clay assumed to have been derived from the underlying sandy loam and ground morainal material due to frost action. It is known that clay contains "inorganic colloidal substances" (10) and that peat consists partly of a "colloidal-complex capable of adsorbing cations from solution" (13). Colloids have strong sorptive power, and Hawkes (9) states that clay minerals and organic matter have the greatest exchange capacity, so that sorption becomes of considerable importance in dealing with soils that are especially rich in these materials.

If sorption phenomena did play a major role in the development of the Tantramar dispersion pattern, then high copper concentrations should be present in the sandy loam [4] (as well as in the peat) and, further, the percentages should be greatest in the vicinity of the water seepages since sorption obeys the law of mass action. While the copper content of the sandy loam is greatest in the vicinity of the seepages, this material contains only 1/5 to 1/10 the concentration of metal found in contiguous forest peat. This indi-

[3] Department of Mines and Technical Surveys, Ottawa, 1956: S = 0.20%. Technical Service Laboratories, Toronto, 1958: S = 0.19%.

[4] The sandy loam contains an appreciable proportion of clay and, hence, inorganic colloidal substances.

cates that either the peat is capable of sorbing five to ten times more copper than can clay, or that some factor other than sorption is responsible for the concentration of the metal in the peat.[5] To credit sorption as the prime factor in the fixation of the copper is therefore unwarranted due to the lack of data. Thus, while sorption may be in actuality the mechanism governing the immobilization of the metal, other factors must also be investigated.[6]

Hydrogen-ion Concentration (pH) and Oxidation Potential (Eh).—The Eh at which most oxidation or reduction reactions take place varies with the pH of the solution. In those reactions concerned with copper minerals, increasing the pH of the system decreases the Eh at which the oxidation can occur. This relationship is well illustrated by Garrels (7, Fig. 2).

The presence of native copper in swamps has generally been ascribed as a response of invading $CuSO_4$ solutions to the environmental pH and Eh with, possibly, microbial activity serving as a catalyst. Forrester (4) has shown that the pH and Eh of the Jefferson City native copper swamp is combatible with Garrels' (7) Cu^0 field.

Conditions in the Tantramar swamp are essentially different. Here, the environment corresponds to the more oxidized zone of Garrels' cuprite field. However, no direct relation of the Tantramar copper substance to the pH and Eh is possible since the metallic compound could not be identified. Nevertheless, certain assumptions can be drawn from the pH-Eh survey of the Tantramar environment; these data are summarized below:

Sector	Soil	pH	Eh (volts)
Clearing	Sandy loam	5.5 to 6.5	0.14 to 0.29
	Forest peat (bank)	6.0 7.2	0.08 0.23
Swampy Forest			
(a) Surface material	Forest peat and humus	4.2 5.1	0.21 0.29
(b) Beneath influence of trees	Forest peat	6.0 7.0	0.06 0.20
Alder Swamp	Sedge peat	5.1 5.9	−.03 −.21
Burnt Upland	Sandy loam	3.6 5.2	0.20 0.34
Normal Forest	Sandy loam	4.0 5.4	0.21 0.32

The reader will note that the pH and Eh of the peat bank and swampy forest, where the bulk of the copper occurs, do not excite comment. An analysis of the environment shows:

1. In the peat bank to alder swamp sequence (5, Fig. 1), there is an increase in acidity under the trees (swampy forest), which is understandable on the assumption that this acidity is due to the formation of humic acids produced by the decay of organic matter newly added to the soil.

[5] Kashirtseva (Int. Geol. Rev., v. 2, no. 1) states that organic matter can "absorb" ten times more copper than can inorganic material. However, he does not differentiate between true absorption (see Hawkes, 4) and copper fixed by the formation of organic complexes (see *Organic Compounds*, below).

[6] Lovering (10) carried out a series of experiments designed to test (among other things) adsorption as a factor in the fixation of copper in the native state. He concluded that adsorption does not play a dominating role in the precipitation of copper in swamps.

2. The alder swamp is slightly more acidic than the peat bank, and there is a marked drop in the Eh to negative values on moving into this sector. The alder swamp smells slightly of H_2S, yet less than one-tenth of one percent copper is present in the decaying sedge peat.
3. The burnt upland and normal forest have similar readings, while the swampy forest is slightly more alkaline and is a little less oxidizing.
4. In the clearing the peat is less oxidizing than the sandy loam, which is what one would expect. However, the pH of the peat bank is greater, the oxidizing effect of which could tend to offset the lower Eh (7, Fig. 2).
5. While the peat bank and that part of the swampy forest beneath the influence of the trees is slightly more alkaline than the other sectors, the little differences in the readings yielded by the peat and sandy loam is such that the pH and Eh association could not possibly be alone responsible for the almost quantitative restriction of the copper to the peat.

Organic Compounds.—Simple copper ions can combine with some naturally occurring organic materials to form "chelate compounds." A common effect of the formation of a chelate compound is to sequester the metallic ion so that it is not available for chemical reaction (9). Some of these compounds may be soluble and some are probably insoluble. However, the nature of these chelate compounds is largely conjectural. The entrapment of copper by the formation of a chelate compound would certainly explain the writer's inability to perform a successful metal separation, as such compounds are often characterized by low specific gravity and low magnetic susceptibility (11).

The fixation of the copper by organic combination is an intriguing possibility but, before it can be fully appreciated, an evaluation of the potentiality of precipitation by microorganisms must be attempted.

Microbiological Factors Affecting Mobility

It has been shown that, during weathering, the copper sulfide minerals are attacked by sulfuric acid and ferric sulfate produced by microbial action on pyrite (2). This process was commercially developed by Kennecott Copper Corporation,[7] the copper being precipitated as "sponge" by cementation with scrap iron. This suggests that a purely inorganic precipitation of copper could explain the Tantramar occurrence if there were an indication that the metal was present in the native state. Three copper swamps are described in the North American literature, and these all contain the copper in the metallic form. The operative processes advocated as responsible for the precipitation of the Cu^0 are: (a) essentially that of the Kennecott patent, i.e. by cementation (4), (b) "by reactions (unspecified) between copper and iron sulfates in the swamp water" (6), and (c) by the reaction of the waste products of bacterial metabolism with a solution of cupric sulfate (10).

[7] United States patent no 2,829,964; cf. Eng. Min. J., 159, 89–91.

Lovering's (10) conclusions are of prime importance in the evaluation of the effect of the Tantramar microbes on the mobility of copper in this swamp environment.

Lovering's aim was to prove that bacterial action, on cupric sulfate in an aqueous medium containing protein, would result in the precipitation of Cu^0. He prepared solutions of cupric sulfate, containing 100 to 500 ppm of copper, and added "a small amount" of bactopeptone as a source of protein. The slow addition of the peptone to the nearly colorless solutions of $CuSO_4$ produced a clear blue color that deepened with the increase of the peptone until a point was reached beyond which no further color change occurred. As the depth of color was proportional to the concentration of copper, Lovering inferred that the color was produced by "the union of copper and organic matter."

The solutions were sterilized, and then some of them were inoculated with the black cupriferous peat from the swamp he studied. The sterile solutions retained their original clear blue color throughout the experiment while the inoculated solutions clouded in 48 hours, changed color from blue to green and, in the course of a few weeks, became dirty gray and heavily charged with flocculent suspended matter. The organic sediment that formed had a pronounced copper color and, under the microscope, proved to consist of innumerable rodlike bacteria and "countless minute spear-shaped flakes having a metallic luster and the characteristic color of copper." Chemical tests identified the flakes as native copper. Lovering then states: "Although the reduction of the cupric sulfate to metallic copper by organic material had been thus proved, the mechanism of the process was not apparent. Two means of reduction are believed to be possible: (a) the waste products resulting from the metabolism of the bacteria might reduce the copper compound to metallic copper, or (b) the copper compound might be consumed by the organisms and broken down by their metabolism, and metallic copper thus precipitated."

To test these two possibilities, Lovering prepared solutions in which the amount of peptone was inadequate to produce the maximum depth of blue color. In these solutions, "containing insufficient bactopeptone to satisfy the copper," bacterial action was so inhibited that at the end of seven weeks they had changed only to the extent of becoming opalescent. "Careful examination revealed the presence of some highly mobile rods . . . suggesting that, although lack of food inhibited their growth, the copper did not have a toxic effect. As bactopeptone consists of a number of organic substances, it is quite probable that some of these substances did not combine with the copper and, as life persisted but precipitation did not take place, it is inferred that the bacteria used material not combined with copper for their food. . . . As no copper was thrown down . . . it appears that the bacteria cannot utilize the copper compound for food. The formation of the copper-carrying sediment (in the first experiment described) suggests that the copper is precipitated as a result of reaction with the waste products of bacterial metabolism and that the copper compound is not to be considered as a direct source of energy that the organism utilizes in its life processes."

The writer performed similar experiments,[8] but with markedly different results. Visual observations were analogous to those described by Lovering apart from the fact that the flocculent, light colored precipitate did not have a pronounced copper color. Under the microscope oval-shaped bodies were observed, which may have been fecal pellets, but no spear-shaped flakes were discernible.

During the experiments, the copper content of the water was determined daily using dithizone in chloroform[9] as an extracting agent, and concomitant pH and Eh readings were taken with a Beckman Model G pH meter. The results of these experiments, following, can only be assigned qualitative values as time was not available to expand the observations by repeated trials.

The pH rose rapidly from about 5½ to 7 in the first five days of the experiments, reaching a maximum of 8 at the termination of the 50 day run. The Eh fell concurrently from 0.4 to 0.3 volts, attaining a minimum of 0.2 volts at termination. The copper in solution during this time decreased at an average rate of:

5 ppm/week for a solution of initial strength	100 ppm Cu
0.6	15
0.03	1

These figures illustrate that the rate of extraction of the copper increased with increased metal concentration in the solution. Also, another trend was noted: in each individual solution, the rates of copper extraction appeared to increase with time. Thus, in each solution, more copper was immobilized in the seventh week than in the sixth week, etc. This is significant as it indicates that the Tantramar peat crumbs, with which the solutions were inoculated, were themselves not responsible for the decrease of copper in the mobile phase; if the metal were removed from solution by sorption to this peat, the rate of removal would certainly not increase with time.

The experimental results may be interpreted in a number of ways, for instance: (a) precipitation of copper by reaction with the waste products of bacterial metabolism, as advocated by Lovering, (b) copper sorption to the bacterial precipitate, (c) sequestration of the copper by the bottom sediments (bacterial precipitate), resulting in the metal being bound organically in a chelate compound.

From the contrasting results evinced by Lovering and the writer, it would appear that the bacteria of the Tantramar swamp play a different role than those of the occurrence studied by Lovering. This is not astounding as the pH of most swamps, including those containing native copper (4), is pronouncedly acidic while the Tantramar peat is subneutral to slightly alkaline. Further, the hydrogen-ion concentrations and oxidation potentials of the writer's solutions[10] fell (as did the Tantramar environment) in the cuprite, rather than native copper, field of stability (7, Fig. 2). Hence, the pH-Eh

[8] A Tantramar peat crumb of ⅛ inch diameter was used to inoculate the solutions of volume 4 liters.

[9] Comparison with similar solutions containing no peptone indicated that the dissolved organic matter did not interfere with the dithizone extraction method of analysis.

[10] Lovering did not measure the pH and Eh during his experiments.

nature of the writer's solutions may well have been different from that prevalent in Lovering's experiments, thus explaining the contrasting results.

To determine which of the above three interpretations is most reasonable appears impossible from the experimental results. Consider the fact that the rate of metal immobilization (a) was greatest in the solution of highest copper concentration (i.e. 100 ppm Cu), and (b) increased in each individual solution with time.

Interpretation No. 1.—As the quantity of bactopeptone in solution was roughly proportional to the amount of metal, then the solution of 100 ppm copper should, and did, exhibit the greatest bacterial action. Also, the activity of the bacteria would increase with time due to microbe multiplication. Thus is supported the suggestion of copper precipitation due to reaction with the waste products of bacterial metabolism (i.e. Lovering's hypothesis).

Interpretation No. 2.—Both the increase in copper extraction with increasing metal concentration and with time support the hypothesis of sorption to the bacterial precipitate. As the phenomena of adsorption and absorption obey the law of mass action, the amount of copper sorbed would be proportional to the metal concentration of the solution, and would also increase with the production of precipitate.

Interpretation No. 3.—The extraction trends also support the possibility of copper sequestration by the bacterial precipitate, thereby forming an organic complex, because the amount of metal held in this manner should be roughly proportional to the concentration of copper in solution and to the amount of bacterial precipitate.

Although the experimental observations are thus not directly applicable to the Tantramar swamp, perhaps qualitative inferences may be drawn: (a) sorption phenomena have previously been shown unsatisfactory in explaining the entrapment process involved in the assimilation of copper by peat, in quantities of up to ten percent, (b) while these experiments appear to suggest that life is a necessity for the extraction of copper from solution, they also indicate that the key to the immobilization of the metal may lie in the bottom sediments (i.e. bacterial precipitate) and that other organic material (such as peat) might render similar results. Because of this it is believed that, rather than crediting the Tantramar microbes as being the sole cause of the partition of copper between the mobile aqueous phase and the immobile solid phase, the possibility of fixation of the metal by organic sediments (peat) should be investigated.

PARTITION OF COPPER

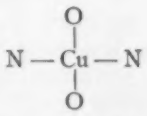
The low sulfur assay (0.2%) precludes the prevalence of the sulfide ion; hence, the black copper sulfide, chalcocite, cannot explain the invisibility of the Tantramar copper compound. The absence of any inorganic mineral of copper is suggested (but not proved) by the writer's failure to separate the metal compound. Further, X-rays taken by Holman of the Geological Survey of Canada did not detect any crystalline metal minerals in the peat (Beschel, personal communication). These facts suggested that the Tantra-

mar copper is in some way bound organically, and so a study of organic compounds of metals was therefore initiated. Two general classes of such compounds are known to occur: namely, organometallic and chelate.

The term "organometallic compounds" is used to denote those substances in which a metal is bonded directly to carbon atoms. While such compounds of copper have been synthesized in the laboratory (16), they had not been discovered in nature by 1943 (8), and a review of the recent chemical and agricultural literature did not reveal the existence of terrestrial organocopper compounds. The only nonsynthetic compounds that might be considered organometallic are those of moissanite SiC and cohenite $(Fe, Co, Ni)_3C$, both of which are found in meteorites. Organometallic compounds are highly reactive and readily decompose in aqueous media; hence, their presence in the Tantramar swamp is most improbable.

The term "chelate compounds" is used to denote these substances in which a metal is bonded directly to nitrogen, sulfur, or oxygen atoms. Chelate compounds of copper are those in which each copper atom is bonded to four donor atoms (either nitrogen, sulfur, or oxygen) in such a way as to produce a square-planar (nontetrahedral) structure. Copper is known to form strong chelate compounds, and their occurrence in terrestrial nature is believed to be not uncommon. Further, they are frequently insoluble in water (11).

As the sulfur content of the Tantramar peat is low (i.e. 0.2 percent), the prime concern is whether the copper will show a preference towards bonding with nitrogen or with oxygen. Sidgwick (17) has shown that copper has a greater affinity for nitrogen than it has for oxygen, and that copper bonded to nitrogen atoms forms chelate compounds more water insoluble than if it were bonded to atoms of oxygen. The copper atoms, however, need not be bound wholly to either nitrogen or oxygen; each metal atom can also be bonded to two nitrogen plus two oxygen atoms, thereby forming the square-planar structure, i.e.



The supposition that the Tantramar copper is chelated allows certain conjectures in regard to the donor atoms. For instance, the assumption that each copper atom is bonded to four nitrogen atoms (since the Cu-N bond forms the most stable chelates) necessitates, of course, that a certain amount of nitrogen be present. As a corollary, the bonding of the copper to two nitrogen plus two oxygen atoms will require less nitrogen (i.e., half as much).

The average composition of peat as estimated by Rankama and Sahama (14) is: 59 C, 6 H, 33 O, and 2 N. To take into consideration the amount of mineral matter in the Tantramar peat, its composition must be modified, as shown below, using the assay of 25 percent carbon as a control (two independent sources[11]). In the following calculation of the number of atoms

[11] Department of Mines and Technical Surveys, Ottawa, 1956: C = 25.30%. Technical Service Laboratories, Toronto, 1958: C = 24.82%.

of nitrogen per atom of copper, it is arbitrarily assumed that 2 percent copper is present in the peat sample. The results reveal that if each copper atom is bonded to two nitrogen plus two oxygen atoms, then all the nitrogen in the peat is combined with the copper in the formation of the chelate.

Element	C	H	O	N[12]	Cu
Weight per cent	25	3	14	0.8	2
Atoms/atom of Cu	66	90	28	2	1

The above calculations imply that (a) where the copper content of the peat falls below one percent, all the metal atoms could be bonded to four nitrogen atoms, (b) between one and two percent copper, oxygen must increasingly substitute for nitrogen, resulting in the metal atom being bonded to two nitrogen plus two oxygen atoms, and (c) above two percent copper, four oxygen atoms would be bonded to part of the copper in the peat.[13]

The inability of vegetation (apart from the resistant moss *Pohlia nutans*) to grow on the bare peat bank of the Tantramar clearing, as contrasted to the floral abundance of the adjoining swampy forest, is thus partly explained. The humus of the swampy forest, which supports the growth of the plants (while overlying peat assaying up to three percent copper), itself contains less than one percent of this metal. Hence, the copper in the humus is likely strongly bound to nitrogen,[14] thus forming a very stable chelate; the copper is therefore less "available" for plant uptake than if it existed as free Cu^{++}. Conversely, the surface peat of the bare peat bank contains up to ten percent copper and, consequently, most of the metal is bound to oxygen thereby forming a considerably weaker chelate. Therefore, the equilibrium between the free cupric ions and the copper immobilized in the chelate favors a higher proportion of cupric ions in the peat bank of the clearing than in the surface humus of the swampy forest; this excess of free Cu^{++} in the clearing precludes the existence of all but the resistant moss *Pohlia nutans*.

The above supports and expands a conclusion of Beschel (1) who, after an exhaustive study of the Tantramar flora, stated simply: "As different methods of extraction (i.e. of chemical analysis) give rather different values and the X-ray analysis revealed no copper minerals in the peat, it is obvious that the copper is chelated or complexed to a high degree. This makes it much easier for the plants to cut down the uptake of the metal."

The acceptance of the copper fixation in the Tantramar peat as being due to a chelation phenomenon demands compatibility with the known facts. Copper bonded covalently to nitrogen and/or oxygen atoms forms stable square-planar chelates, and these have low magnetic susceptibilities; further, their color may be black or brown (15). A color of this sort would explain the invisibility of the Tantramar copper, and the low magnetic susceptibility would account for the failure of the isomagnetic separator to yield a segregation of the copper compound. Also, the binding of the copper organically

[12] Atoms N/atom Cu = (wt. % N/atomic wt. N) (atomic wt. Cu/wt. % Cu).

[13] As the amount of nitrogen was not obtained by analysis, but was inferred from the known amount of carbon in the peat, these relationships and the indicated percentages have only a qualitative significance.

[14] Humus contains 1½ to 3 times more nitrogen than does peat (14).

would prevent the settling of the copper compound in the heavy bromoform liquid of Sp. Gr. 2.89.

It is realized that the evidence is insufficient to state that "the Tantramar copper is predominantly chelated." However, the Tantramar environment does not preclude the presence of a copper chelate. Consider the following statement (11): "The equilibrium involving the formation of metal chelates indicates a competition between the metal and hydrogen ions. Hence, the more stable the chelate, the lower the pH at which it is capable of existing." The pH of the Tantramar peat varies roughly between six and seven; therefore, abundant hydrogen ions are not available to compete with the copper for the chelating agent.

Martell and Calvin (11) further state that: "In general, the data indicate a considerable increase in the oxidation potential as a result of complex[15] formation. It is apparent that, in general, coordination with a donor group increases the oxidation potential and hence increases the relative stability of the higher valence state.[16] This is particularly true of combination with negatively charged donors." In a study of the Tantramar environment, it was noted that the oxidation potential of the copper-containing peat averaged + 0.2 volts, and the muck in the alder swamp − 0.1 volts. Again, it is found that the facts do not oppose the chelation possibility since (a) the copper-rich peat (3 to 10% Cu) is marked by a relatively high oxidation potential, (b) the low amount of this metal in the muck of the alder swamp (less than 0.1% Cu) is linked with a low oxidation potential, and (c) the formation of a chelate tends to increase the oxidation potential. While these three facts may be unconnected and the apparent relation fortuitous, at least they cannot be said to contradict the chelation hypothesis.

It was mentioned earlier that the presence of cuprous oxide was not disproved and, as can be seen from Garrels' diagram (7, Fig. 2), the pH-Eh association in both peat and sandy loam does not preclude the existence of Cu_2O. The failure to obtain a separation of cuprite from the peat indicates that it either is not present or is too finely divided to sink in the bromoform liquid, in spite of its superior specific gravity. If the largest size of the cuprite particles were less than 0.06 mm, the grinding would not have freed the heavy oxide from the enclosing peat crumbs, effectively prohibiting separation. Thus, it is not possible to state whether Cu_2O is or is not the dominant form of the copper in the peat. It must be remembered, however, that the attempts aimed at separating the copper substance from the peat were carried out on surface material from the bare peat bank. This material contains up to 10 percent copper and, hence, if the copper were chelated, the compound so-formed would be relatively unstable, resulting in a higher proportion of free cupric ions (i.e. relative to the copper contained in the humus of the swampy forest). Consequently, if cuprite is the dominant form of the copper in the swamp, it would be more apt to appear in the surface peat of the bare peat bank. Because Cu_2O was not identified in this material, and because the X-ray laboratory in Ottawa failed to detect any crystalline metal minerals in

[15] This includes chelation.
[16] i.e. Cu^{++}.

the peat, it is believed that the most likely form of the copper is that of a chelate.

Lack of data on the Tantramar microorganisms prevent the determination of their effect on the mobility of the copper in the Tantramar environment. However, as microbes apparently have not been shown to be capable of the assimilation and concentration of copper in quantities approaching that contained in this peat, it is assumed that the only possible value that can be assigned to their activity is that of a catalytic effect, speeding the formation of the copper compound already stable under the chemical conditions imposed by the environment.

Hence, it is concluded that, of all the factors investigated that may have been operative in the determination of the behavior of copper in the Tantramar environment and its partition between the mobile aqueous phase and the immobile solid phase, the organic sequestration of the metal by peat appears to be the most credible. This process would thus account for the concentration of copper in the organic sediments to the relative exclusion of this metal in the sandy loam and ground morainal material. This conclusion finds support in a statement by Mason (12), in reference to the principles governing the concentration of the minor elements in biogenic deposits: "Another significant process is . . . chelation of metallic ions by complex organic molecules; experiments have shown that humus (and presumably also peat) has a considerable capacity for (extracting) a variety of cations from solution and retaining them in stable combination."

SUMMARY

Solutions containing dissolved copper percolated upward through the glacial material, emerging as seepages in the clearing, and the metal was immobilized in the forest peat. The dispersion pattern is clearly dependent on the distribution of the organic matter, the drainage only exerting a secondary effect. The chief factors affecting the mobility of the metal appear to be diffusion, capillarity, evaporation, the growth of frost crystals, and the formation of organic copper compounds. The solubility of salts, coprecipitation, sorption, the hydrogen-ion concentration and oxidation potential, and the action of plants and microorganisms all seem to have played only minor roles in the determination of the Tantramar dispersion pattern.

In a comparison with other copper swamps, it is shown that, in many ways, the Tantramar occurrence is unique. The normal situation appears to be visible native copper in a swamp of acidic pH. The Tantramar peat, on the other hand, is subneutral to slightly alkaline and the presence of mineralization, in spite of copper in quantities up to ten percent dry weight, is not at all apparent due to the invisibility of the metal compound. The Tantramar copper does not appear to be in the native state, nor can finely divided black chalcocite hold the answer to the mineral's obscurity as the low sulfur assay (0.2%) precludes the prevalence of the sulfide ion. The failure of attempts to separate the copper substance and the inability of X-rays to detect any crystalline metal minerals in the muck indicate (but do not prove) the ab-

sence of any inorganic mineral of copper. These facts may imply that the Tantramar copper is in some way bound organically.

It is suggested that the copper is sequestered by the organic constituents of the Tantramar peat, forming a chelate compound in which the metal is bonded to nitrogen and oxygen. While such a mechanism has not been definitely established as responsible for the immobilization of the metal, the facts at hand are compatible with this preferred hypothesis, which not only accounts for the invisibility of the copper substance but also explains its inferior specific gravity and low magnetic susceptibility.

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POSSIBLE MASKED HEAVY MINERAL DEPOSIT, FLORIDA PANHANDLE[1]

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ABSTRACT

Analysis of about 400 sand samples, from the vicinity of the Apalachicola River delta (Florida Panhandle), raises the question of where the river-carried minerals are being accumulated. The river apparently has been delivering a larger quantity of heavy minerals than is found on the surface of the modern beaches and barrier islands. Coastal energy conditions are such, however, that a relative increase in heavy mineral content should be observed on the rim of, or immediately offshore from, the delta.

In the light of an anomalous distribution of coarse and fine quartz sands, on the offshore shoals of the area, the hypothesis is developed that the heavy mineral content of the shoals increases significantly with depth. If the reasoning is correct, the shoals might be attractive ventures for commercial development.

INTRODUCTION

THE Chattahoochee-Apalachicola river system drains the crystalline complex of the southern Appalachian Mountains, in Georgia and Alabama, and delivers its load across the panhandle of Florida to the northeastern shore of the Gulf of Mexico. Inasmuch as it carries a considerable quantity of heavy minerals, some of commercial importance, it would be of interest to know how it distributes its load and where this material comes to rest.

Heavy mineral accumulations are known along the Atlantic coast of the southeastern states. These minerals were likewise derived from the southern Appalachian Mountains, transported by rivers, and distributed along the beaches. Mining of the Atlantic coast heavy minerals is well-developed; however, no mining of the Florida Panhandle heavy minerals is known.

The work reported here is part of a larger project, carried out under the direction of the senior author, on the near-shore morphology and sediments along the Florida coast. Initial field work was done in 1955, and the over-all project has been in operation ever since. A summary report of general conclusions, based on the first five years of work, has been published elsewhere (4).

Contributing also to this paper are certain results of an investigation for heavy minerals conducted by Coastal Petroleum Company on its State of Florida tidelands oil, gas and mineral leases on the west coast of Florida. This project was supervised by the third author. The two projects, however, were closely coordinated.

[1] Certain data published by permission of Mr. Benjamin W. Heath, President, Coastal Petroleum Company.

Field and equipment costs for the university project have been borne by the Florida State University Research Council, Florida Board of Conservation, Florida Geological Survey, and Coastal Petroleum Company. This support is gratefully acknowledged. The Company conducted its field project with advice and guidance from the senior author, his associates at Florida State University, the Florida Geological Survey, and the local office of the U. S. Bureau of Mines, all of which is similarly acknowledged.

GENERAL SETTING

Florida Panhandle coastal energy levels increase in a westerly direction (Fig. 1). The "Big Bend" (eastern end of the Panhandle) is marked by what is essentially zero energy; the average breaker height is much less than 10 cm, and approaches zero. At Cape San Blas the average breaker height is about 12 cm. In the vicinity of Pensacola, near the western end of the Panhandle, the average breaker height is about 25 cm. The mouth of the Apalachicola River is roughly at the division point (10 cm breaker height) between the low-energy coast, to the east, and the moderate-energy coast to the west.

Because the energy is increasing in the down-drift direction (toward the west), it might be reasoned that the river load is put immediately into the littoral drift, carried westward for some appreciable distance, and then either accumulated locally or scattered across the shelf. The estimated load carried by the river is great enough, however, that at no point along the west or panhandle coast of Florida is the energy level adequate to transport it. The load is, therefore, being deposited near the river mouth, in one form or another, except for solution load (which has not been investigated) and the finer part of the wash load (which is carried westward, in good part, by the prevailing drift). The Apalachicola delta area, then, should be a promising area for heavy mineral exploration.

The numerous beach ridges on the western part of the delta and on some of the barrier islands indicate that the delta is prograding (that is, that river load markedly exceeds capacity of the littoral drift). The volume of sand included in the beach ridges is about 6×10^6 m^3 (much less than one per cent of a cubic mile).

Barrier islands, and spits of similar size, rim the delta. These become discontinuous eastward, where there is neither any appreciable quantity of sand nor a sufficiently high energy level to require much sand. They change character at about the western edge of the delta. Along the delta rim, barrier islands contain about 1.7×10^9 m^3 of sand (about one-half cubic mile).

Inasmuch as the barriers rest on a sand base that is below sea level much of this sand could not be processed by ordinary dry-land methods but could be recovered by fresh-water or marine methods.

Seaward from the barrier islands are three large, well-developed shoal systems (6, 7). These occur near the southeastern edge of the delta (off Alligator and Lighthouse Points), near the middle of the south rim of the delta (off Cape St. George), and near the southwestern edge (off Cape

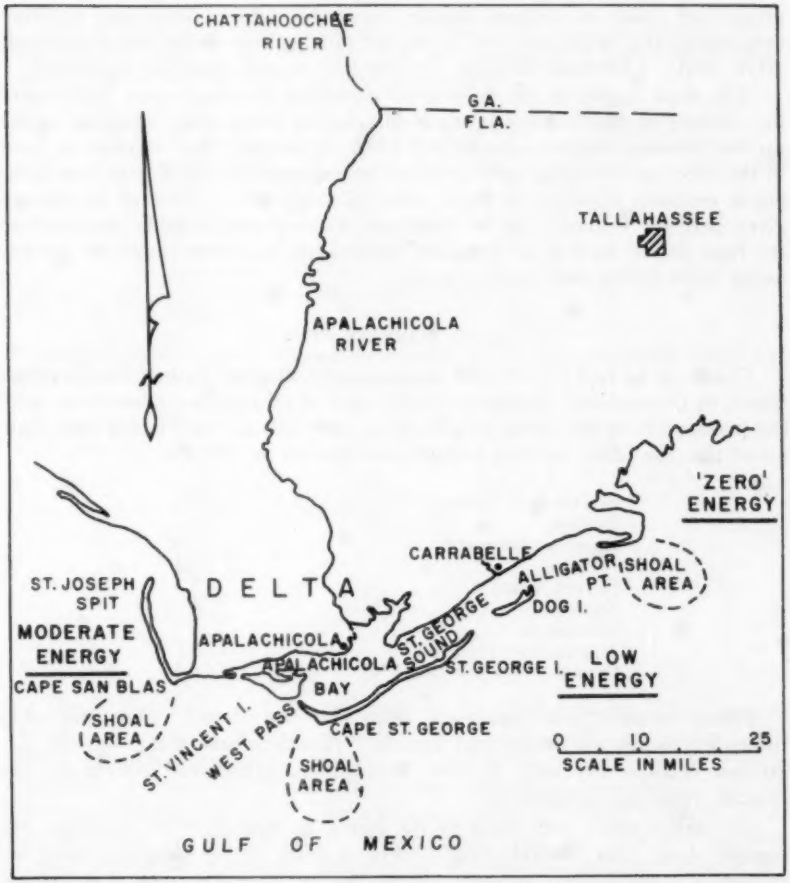

FIG. 1. The delta of the Apalachicola River, and adjacent areas in the Florida Panhandle and the Gulf of Mexico. The energy level increases from approximately "zero" (as measured in terms of breaker heights) in the eastern part of the map, to the "moderate" category (annual average breaker height exceeding 10 cm) in the western part of the map. Three large off-shore shoal complexes are shown. Their positions may be due, in part, to former locations of the river mouth, and hence to former sites of accumulation of sand. The present active outlet from Apalachicola Bay is through West Pass, into a shallow topographic basin between the Cape St. George shoal and the Cape San Blas shoal.

San Blas). The three shoals together probably include nearly 2×10^9 m^3 of sand (about one-half cubic mile). Of the three, the eastern shoal is thought to contain the least sand, and the middle shoal the most (perhaps as much as 1.0×10^9 m^3). These shoals are also evidence that the coast is

prograding (that is, shifting slightly seaward). All of this sand is, however, completely below sea level, in waters ranging from about one m to about 20 m deep. This sand could be recovered by marine dredging equipment.

The sand supply in the delta area, excluding the sand sheet that covers the surface of the delta proper, is about one cubic mile, roughly evenly divided between barrier islands and offshore shoals. The volume of sand in the sheet on the delta surface cannot be estimated without bore-hole data, but is probably of about the same order of magnitude. None of the figures given here for volumes can be considered as absolutely reliable inasmuch as the base of the sand is an irregular surface, as has been shown in several water wells drilled onshore in the area.

HEAVY MINERAL SUITE

Cazeau and Lund (2) studied the bed load sediments of the Chattahoochee River, in Georgia and Alabama. For a total of 22 samples, taken from near the headwaters in the north to almost as far south as the Florida line, they found that the heavy mineral content was divided as follows:

Hornblende (green)	28%
Epidote	19
Ilmenite, magnetite	14.4
Kyanite	14.1
Garnet (pink)	5.5
Staurolite	5
Leucoxene	4
Tourmaline (brown)	3.7
Others	6.3

Heavy minerals that increased, relatively, downstream, were monazite, rutile, leucoxene, staurolite, and kyanite. Monazite and rutile showed the greatest relative increase. Epidote, hornblende, garnet and sillimanite decreased, relatively, downstream.

A detailed study was made of the heavy mineral suite of the Cape St. George shoal (the central shoal). For a total of 38 samples, taken at corners of a grid having one-mile spacing, heavy mineral content was divided as follows:

Ilmenite, magnetite	33.0%
Epidote	12.1
Kyanite	12.0
Staurolite	6.5
Sillimanite	6.4
Hornblende	5.8
Leucoxene	5.7
Rutile	5.7
Zircon	4.9
Tourmaline	4.1
Garnet	1.3
Monazite	1.3
Others	1.2

Ten Coastal Petroleum Company samples averaging 1.2 percent heavy minerals, not taken on the one-mile grid, and processed in a slightly different manner, contained the following heavy minerals:

Ilmenite, magnetite including leucoxene	39.7%
Kyanite	11.7
Staurolite	8.3
Epidote	7.7
Rutile	6.7
Zircon	5.7
Tourmaline (brown)	5.4
Monazite	5.3
Hornblende (blue-green)	4.0
Others	5.5

Seven beach samples, spaced irregularly along the panhandle coast (3) yielded the following relative abundances:

Hornblende	18.7%
Kyanite	16.4
Tourmaline	14.7
Sillimanite	11.2
Ilmenite, magnetite	10.3
Staurolite	8.9
Leucoxene	7.2
Zircon	2.1
Rutile	2.1
Others	8.4

HEAVY MINERAL QUANTITIES

The total quantity of heavy minerals in the Chattahoochee River samples averaged less than 2 percent by weight (2), decreasing downstream. Ten samples collected from the lower reaches of five rivers crossing the Florida Panhandle averaged 1.38 percent heavy minerals; seven beach samples averaged 0.10 percent (3). The average quantity of heavy minerals in 38 samples taken on the Cape St. George shoal (Fig. 2) was 0.48 percent. Coastal Petroleum Company obtained 77 samples in the same area which averaged 0.43 percent, whereas 17 samples east of the shoal averaged 0.15 percent. Heavy minerals made up only a trace of submarine sand samples collected off Dog Island.

Local variations in heavy mineral content were great, ranging from a trace to about 2 percent. In St. George Sound, heavy mineral content of 46 samples decreased eastward from a maximum of 0.55 percent near the mouth of the river. A significantly large clay component prevented satisfactory laboratory separation of heavy minerals from samples taken in Apalachicola Bay, but a single bay beach sample (composed largely of sand) yielded 0.46 percent heavy minerals. (Skims on the beaches yielded much higher figures but represent limited amounts of material.)

Most of the water, and sediment load, delivered by the Apalachicola River, is channeled into the Gulf through West Pass (between St. George

and St. Vincent Islands). A bottom sample taken about one mile south of West Pass contained 0.8 percent heavy minerals. Other bottom samples taken within a radius of three miles, to the south and west of the pass contained no more than 0.4 percent heavy minerals. It is probable that former passes through St. George Island have discharged sediments farther east.

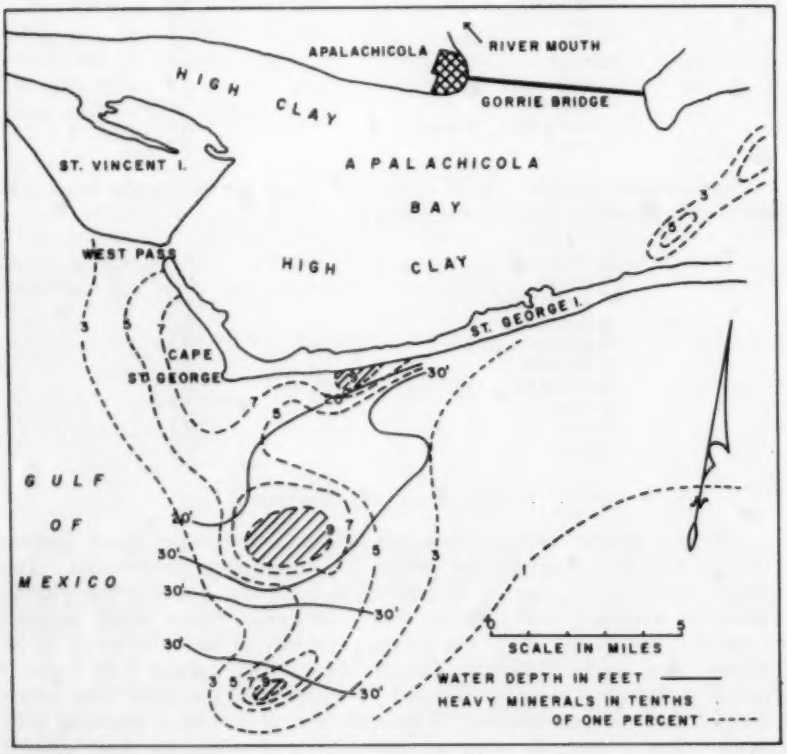

FIG. 2. Generalized heavy mineral distribution in the vicinity of the Cape St. George shoal. Depths are given in feet (solid lines), and total heavy mineral concentrations in tenths of one per cent (dashed lines). For the latter isopleths, moving averages were contoured, in an effort to show distributional trends rather than erratic local figures. This map is based on 162 samples.

The largest proportion (by weight) of heavy minerals obtained from the Cape St. George shoal was 1.9 percent. Of the 38 samples collected on this shoal system, five contained more than 1.0 percent heavy minerals, and two of these exceeded 1.5 percent. These five "rich" samples were taken from three areas: (a) a shallow-water strip parallel with and within a half mile of the beach; (b) a broad single swell about five miles offshore; and

(c) the south flank of the shoal area, about eight miles offshore. The general trend (obtained from the 38 samples) is for the heavy mineral content to be greater in finer sand, in shallower water, and toward the west. Similarly, of the Company's 77 samples on the shoal, nine were over 1.0 percent and two over 1.5 percent.

The method of laboratory separation of Coastal Petroleum Company heavy mineral samples has been described elsewhere (1).

DISCUSSION

Heavy minerals in the area decrease, in absolute abundance, downstream. In relative proportions there is a shift that results in less stable types dominating upstream, more stable types downstream. The same general situation is thought to hold for the rivers and beaches along the Atlantic coast of the southeastern states.

The two areas differ greatly in the available methods whereby heavy minerals are concentrated. Along the east coast, energy levels are high to moderate, *de*creasing in a southerly direction from Cape Hatteras (N. C.) to approximately the vicinity of Jacksonville (Fla.). This southward decrease is responsible for the accumulation of large shoals of sand off the North Carolina coast. Most of the heavy minerals that are moved southward along this part of the Atlantic coast were probably delivered to the shore in South Carolina and Georgia (5) and therefore would not be expected in the North Carolina shoals, but instead should be incorporated in coastal sediments in the general vicinity of Jacksonville. Sea level fluctuations throughout the Pleistocene would have the effect of widening (in an east–west direction) the belt of accumulation. Further south, energy levels increase again, and hence heavy mineral accumulations are not thought likely there.

The sand deposits off the mouth of the Apalachicola river have been built up, despite a down-drift *in*crease in energy levels, as a result of the fact that the transporting capacity of the river appears to exceed that of the drift. The heavy minerals should be trapped in the same way as the quartz sand, and perhaps more efficiently. Therefore large concentrations should be available in the area. The surface-sampling results described in an earlier paragraph do not seem to bear this out.

The three shoal areas off the Apalachicola delta are of a type which has been subjected to very little previous study. Each shoal complex is made up of several more-or-less parallel ridges (or swells) and furrows (or swales). The relief is very gentle, commonly being of the order of a few meters per kilometer. The water depths are typically one to 10 m on the swells, and six to 20 m in the swales. Ordinarily we would expect that the sands on the swells would be partly winnowed of fines, and that the coarser grains would have accumulated in a sort of lag sand. A careful study of grain-size distribution, however, shows that the sands on the swells are relatively fine-grained, whereas the sands in the swales are relatively coarse-grained. This cannot be explaind in the usual terms of winnowing.

Each shoal complex is the point of considerable refracted wave attack. The local load-energy imbalance maintains the shoals in the face of this attack, but under storm conditions considerable rearranging of the shoals must take place. A bottom topography map, made during the course of the present study, differed considerably from the available U. S. C. and G. S. chart (No. 1262, based on soundings in general 50 or more years old).

It is therefore reasoned that temporary high-energy wave trains (during storms) reworked portions of the shoals, and that, during settling of the materials, the heavy minerals were concentrated near the base of the redeposited sands, along with the coarser quartz grains. Such a mechanism would leave relatively fine grained, relatively pure quartz sands (that is, with low heavy mineral content) in the upper layers. If this hypothesis is correct sand-surface sampling in such an area will not provide a measure of the volume of heavy minerals present. Instead, bore-hole samples will have to be obtained, down to the desired maximum depth, for further study. Areas, such as this shoal, in which bottom samples indicate higher than average heavy mineral content, would be the most likely places for deeper sampling.

CONCLUSION

One or more cubic miles of quartz sand are included in the Apalachicola River delta, associated barrier islands, and offshore shoals. Sand-surface samples in the area generally yield less than one percent (by weight) of heavy minerals. The largest concentrations (between one and two percent) occur on the offshore shoals. It is reasoned that the heavy mineral content increases with depth in the shoal sands, but no exploration program has been undertaken, as yet, to test this hypothesis. If this concept is correct, concentrations in excess of four per cent should be encountered within about five meters of the sand surface and within about 10 m of the water surface. It is possible that the middle shoal alone contains about 4×10^7 m^3 of heavy minerals, including perhaps 2×10^6 m^3 each of rutile and zircon and about 5×10^5 m^3 of monazite. The western shoal, although smaller volumetrically, may also contain large quantities of heavy minerals. The eastern shoal, the smallest of the three, is thought to consist essentially of quartz and shell fragments. It is thought that the barrier islands, although more easily accessible, are not as rich in heavy minerals as the middle and western shoal area.

Florida State University,
Tennessee Valley Authority,
Coastal Petroleum Co.,
March 28, 1961

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THE STRATIGRAPHIC SUCCESSION AND STRUCTURE IN THE ZINC CORPORATION LTD. AND NEW BROKEN HILL CONSOLIDATED LTD., BROKEN HILL, NEW SOUTH WALES

D. S. CARRUTHERS AND R. D. PRATTEN

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ABSTRACT

Since the last comprehensive analysis of the geology of the Broken Hill ore deposit was published in 1953, important changes have taken place in the interpretation of the stratigraphic succession and structure of the deposit and its environs. These changes have resulted principally from the greater amount of information now available from diamond drilling.

The various conformable ore layers making up the deposit in the two mines are confined to a stratigraphic thickness averaging 300 to 400 feet, approximately in the middle of a sequence of beds (of Precambrian age) known as the Mine Sequence. The top and bottom members of the Mine Sequence are granitic gneisses, and between these lie principally sillimanite-garnet gneisses, amphibolites, "Potosi" gneiss, and the ore-bearing layers themselves. The thickness of the sequence between the granitic gneisses is estimated to be 2,000 to 2,500 feet.

The principal structural element is a major syncline, the Hanging Wall Basin. Previous interpretations (particularly those of Gustafson, Burrell and Garretty published in 1950, and King, Thomson and O'Driscoll published in 1953) depicted the granitic gneisses as one and the same stratigraphic member, and the structure between them, on the eastern side of the Hanging Wall Basin, as being anticlinal. It is now shown that the granitic gneisses are separate members, and that the sequence be-

tween them, containing the ore deposit, occupies the eastern limb of the Hanging Wall Basin. Other distinctive beds such as amphibolite, "Potosi" gneiss and bedded iron formation, previously thought to be unique in the sequence, also occur at more than one stratigraphic level. The ore bodies are associated with, but not necessarily localized by, a major drag fold that clearly indicates tops facing west.

INTRODUCTION

THE Broken Hill ore deposit in western New South Wales had produced, to the end of 1960, some 86 million tons of ore, containing 11.2 million tons of lead, 7.6 million tons of zinc, and 633 million ounces of silver. It is almost continuously stopable over a length of 20,000 feet, and has a vertical extent of up to 2,000 feet.

The deposit is conformable with the enclosing highly metamorphosed Precambrian sediments. For three-quarters of its known length, all ore has been produced from two parallel, folded conformable layers or beds. In The Zinc Corporation Limited and New Broken Hill Consolidated Limited, there are as many as six of these ore-bearing beds, the other four having made their appearance stratigraphically above the first-mentioned two.

The Zinc Corporation Limited and New Broken Hill Consolidated Limited mines occupy the southern portion of the mining area, and the ore bodies of these two mines cover a known length of nearly 6,000 feet. To the end of 1960 these two mines had produced some 23 million tons of ore of average grade 13.6 percent lead, 3.1 ounces silver per ton, 11.2 percent zinc. At present rates of production, these two mines are responsible for about two-thirds of the annual ore production from Broken Hill.

The last comprehensive analysis of the structure and stratigraphic succession in the Broken Hill mines was published in 1953 in "Geology of Australian Ore Deposits," by H. F. King, B. P. Thomson and E. S. O'Driscoll (8, 9, 10), the work for this publication being largely completed in 1951. King, Thomson and O'Driscoll paid tribute to the work of J. K. Gustafson, H. C. Burrell and M. D. Garretty, who from 1936 to 1939 made a most detailed and comprehensive study of the Broken Hill deposit and its environs. The results of this study were available to the mining companies in 1939, but were not published until 1950. The accomplishments of Gustafson et al. included the first systematic mapping of underground exposures and this led to the recognition of one of the basic facts of Broken Hill ore occurrence: two principal ore types form continuous layers of stratigraphic habit. This was fully confirmed by the 1946–51 mapping of subsequent exposures and, as a result, the interpretation of the stratigraphic succession and structure worked out by Gustafson, Burrell and Garretty (4) (working as the "Central Geological Survey") was largely retained, with some important modifications, in the 1951 analysis.

Since then, much diamond drilling has been done in the Broken Hill mining area and its extensions, and particularly in The Zinc Corporation Limited and New Broken Hill Consolidated Limited. The present paper presents the most recent picture of the stratigraphic succession and structure,

and incorporates much that was known up to 1951, as well as new information provided by diamond drilling and underground geological mapping since that time.

It had been inherent in the 1939 and 1951 interpretations that each of the distinctive rock types in the sequence represented one unique stratigraphic member. Thus, the granitic gneiss, amphibolite, bedded iron formation and "Potosi" gneiss were each thought to occur in only one stratigraphic position. As a result of the restriction which this placed on interpretation, the structure containing the ore deposit had to be regarded as an anticline. Subsequent diamond drilling has shown that the distinctive rock types (granitic gneiss, amphibolite, bedded iron formation and "Potosi" gneiss) are not unique; each occurs at more than one horizon. As a result of this discovery, the interpretation of the structure has been relaxed, and the group of beds containing the ore deposit is seen as occupying a position on the eastern limb of a major syncline known (since Gustafson's time) as the Hanging Wall Basin.

SOURCES OF INFORMATION

In addition to the publications of Gustafson, Burrell and Garretty, (4, 6, 7), and King, Thomson and O'Driscoll (8, 9, 10), information for the present interpretation was obtained from a number of sources. Surface mapping of The Zinc Corporation Limited and New Broken Hill Consolidated Limited leases has been done principally by—

E. C. Andrews (1)	400 feet to an inch (1922)
Central Geological Survey	100 feet to an inch (1936 to 1939)
The Zinc Corporation Limited	400 feet to an inch (1946 to 1948)

For the newer information, and for a better understanding of the older information, the authors have had available much diamond drill core, and mapping of underground exposures accumulated over the last ten years. It is significant that up till 1939, when the Central Geological Survey finished its work, there were no drill holes that covered the sequence from the ore bodies to either the eastern or western granitic gneisses. (The average horizontal distance between the granitic gneiss layers is 3,000 to 4,000 feet.) In The Zinc Corporation Limited and New Broken Hill Consolidated Limited we now have five holes which have been drilled from the mine workings to the eastern (or lower) granitic gneiss, and one from the mine workings to the western (or upper) granitic gneiss. Also in New Broken Hill Consolidated Limited there is one surface drill hole that covers the entire sequence between the lower and upper granitic gneisses.

In about 1940 six holes were drilled in the central part of the field, in ground now held by Broken Hill South Limited. These were drilled to the east of and below the ore body, and at least four of them intersected the eastern granitic gneiss. This was not realized at the time however, and the cores were missing for a considerable time, not becoming available again until 1954. In 1956 B. R. Lewis, Chief Geologist of Broken Hill South Limited, recognized the significance of these intersections of granitic gneiss,

and he was the first to propose that the eastern granitic gneiss lies with tops facing to the west. He pointed out that in view of this, the eastern and western granitic gneises could not represent the same bed, and that all the beds between them have tops facing west—i.e. the structure is not an anticline, but a limb.

The exploratory drilling which has been done since 1939 has provided us with an excellent picture of the sequence of beds between the granitic gneisses —a picture that was not available to the Central Geological Survey. Their interpretation made good structural sense in terms of the information existing in 1939. It has become inadequate only because of the much greater amount of information that we now have.

THE STRATIGRAPHIC SUCCESSION

General

As already pointed out, the diamond drilling done since 1939 has shown that there is repetition of the distinctive rock types such as granitic gneiss, amphibolite, bedded iron formation and "Potosi" gneiss in the stratigraphy. Thus the change from the stratigraphic succession of Gustafson et al. (6), has been a change towards complexity of the succession, accompanied by a change towards simplicity of the structure.

Exploratory drilling has tested the full width of the succession on a number

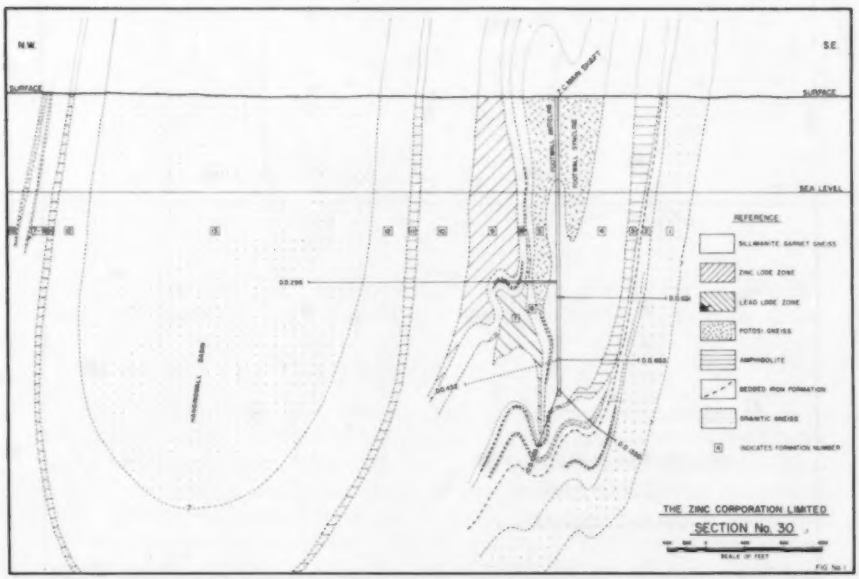

FIG. 1.

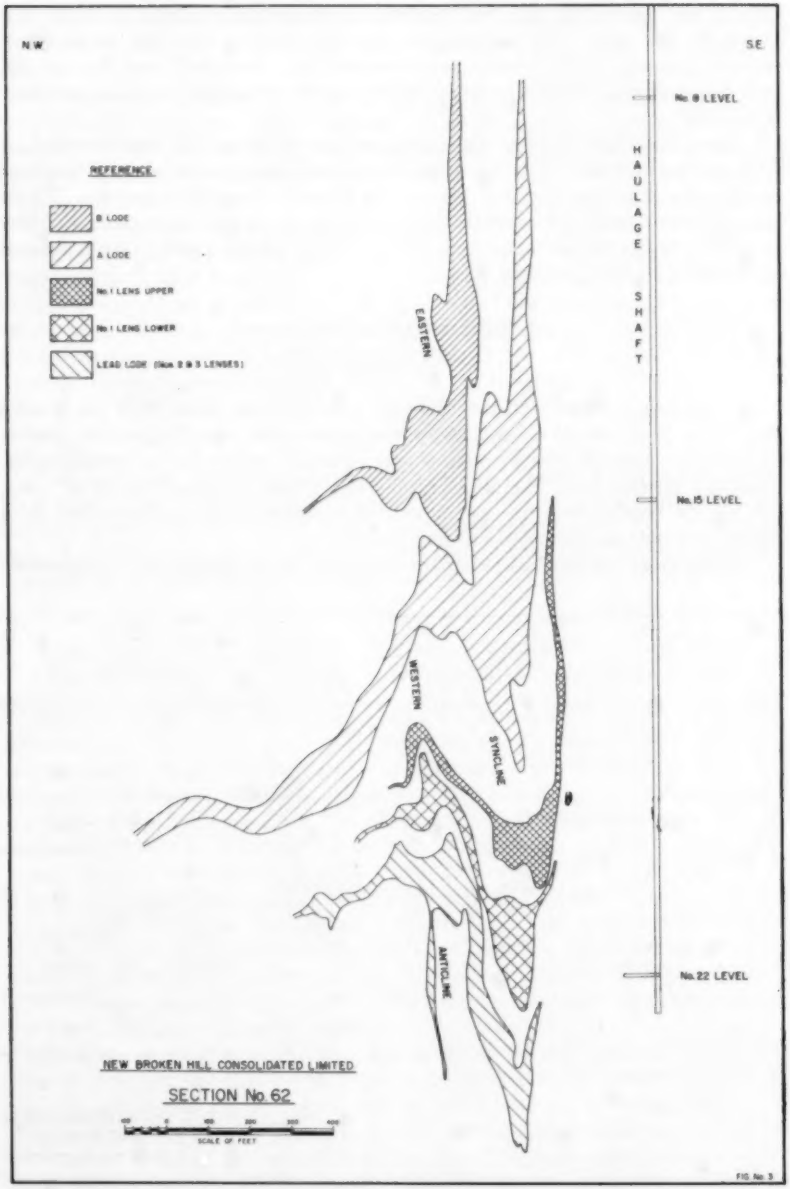
N.W
S.E
No. 8 LEVEL
HAULAGE SHAFT
No. 15 LEVEL
No. 22 LEVEL
REFERENCE
B LODE
A LODE
No. 1 LENS UPPER
No. 1 LENS LOWER
LEAD LODE (Nos. 2 & 3 LENSES)
EASTERN
WESTERN
SYNCLINE
ANTICLINE
NEW BROKEN HILL CONSOLIDATED LIMITED
SECTION No. 62
SCALE OF FEET
FIG. No. 3

FIG. 2.

of cross sections in The Zinc Corporation Limited and New Broken Hill Consolidated Limited. Figure 1 (Section No. 30, at The Zinc Corporation Limited Main Shaft) illustrates the present interpretation of the stratigraphic succession and structure. Figure 2 (a cross section in Broken Hill South Limited just north of The Zinc Corporation Limited boundary) is Section C-C in Gustafson et al. (6) and illustrates the interpretation adopted by them in 1950. Unfortunately a fully interpreted version of The Zinc Corporation main shaft section was not produced in the 1950 paper, so that the nearest available section (C-C—Figure 2 in this paper) has been reproduced for the purposes of comparison. Figure 3 (Section No. 62, at New Broken

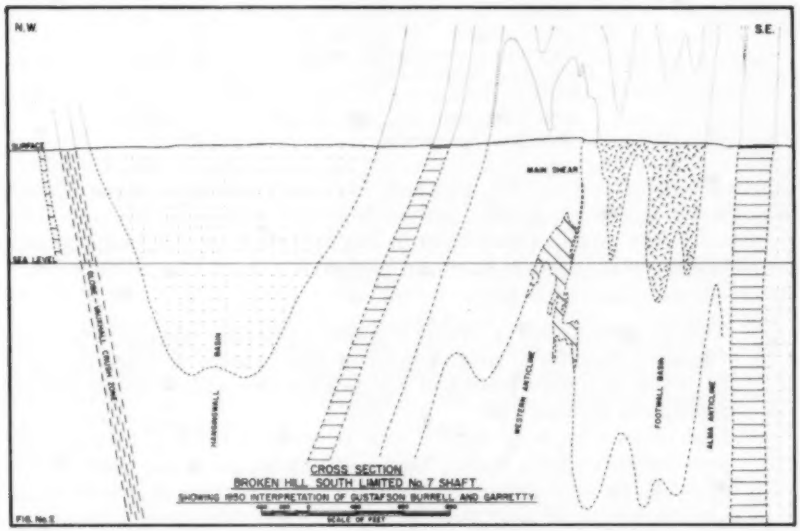

FIG. 3.

Hill Consolidated Limited Haulage Shaft, 2000 feet south of Section No. 30) shows the sequences and structure of the ore-bearing layers in more detail.

Description of Formations

No. 1.—Lower granitic gneiss. This is the eastern granitic gneiss at the surface and is the lowest stratigraphic member intersected by drill holes in the Mine Sequence. It consists of platy, medium to coarse grained quartz-felspar (orthoclase and plagioclase)-biotite gneiss, with garnet in places. Where garnet is abundant, as it may be in the upper portion of the formation, the rock somewhat resembles "Potosi" gneiss. Thickness at the surface along most of the line of lode area varies from 200 to 600 feet, an average figure in The Zinc Corporation Limited and New Broken Hill Consolidated

SUMMARY OF THE STRATIGRAPHY OF THE MINE SEQUENCE

Formation No.	*Brief Description*
13	Upper granitic gneiss
12	Sillimanite-garnet-biotite gneiss
11	Upper amphibolite
10	Sillimanite-garnet-biotite gneiss and quartzite, locally with "Potosi" gneiss
9	Zinc lode formation
8	Quartzite and garnet-biotite-sillimanite gneiss, with No. 1 lens lode horizons, and locally, "Potosi" gneiss.
7	Lead lode formation
6	Sillimanite-sericite-garnet-biotite gneiss with calc-silicate ellipsoids
5	"Potosi" gneiss
4	Sillimanite-garnet-biotite gneiss with calc-silicate ellipsoids
3	Main lower amphibolite
2	Sillimanite-garnet-biotite gneiss with thin layers of bedded iron formation, amphibolite and "Potosi" gneiss
1	Lower granitic gneiss

Limited being 350 feet. No drill hole has penetrated more than 270 feet into the lower granitic gneiss.

No. 2.—The principal rock types in this formation are sillimanite-garnet-biotite gneiss, and quartzite bands up to one foot thick. In addition there are—

a. Two or three bands of "Potosi" gneiss (generally more siliceous and felspathic than the main underwall "Potosi" gneiss of Formation No. 5). The best developments of this rock are generally below the eastern syncline of the lead lode.
b. One or two bands of bedded iron formation (B.I.F.), a magnetite-quartz-garnet-apatite rock. This is the most persistent development of B.I.F., in the sequence, being known over a distance of several miles.
c. One or two bands of amphibolite generally less than ten feet thick.

The thickness of Formation No. 2 is very variable. In the eastern limb opposite the ore bodies on Section No. 30 it is as little as 100 feet thick, while below the ore bodies it appears to reach a thickness of 600 feet.

No. 3.—The main lower amphibolite. The amphibolites in the sequence usually consist of hornblende, pyroxene, plagioclase and garnet. They are commonly well banded, and this banding is always parallel to the bedding in the enclosing gneisses. Some parts of the amphibolite layers consist of quartz-felspar-garnet-biotite granulite phases. In places this granulite is hardly distinguishable from phases of "Potosi" gneiss. Formation No. 3 varies from 20 to 200 feet thick where intersected by drilling, and may be as much as 300 feet thick in places on the surface. It shows a general tendency to become much thinner as it passes underneath the ore bodies.

No. 4.—Sillimanite-garnet-biotite gneiss with numerous thin (up to one foot) bands of quartzite, and calc-silicate ellipsoids. The ellipsoids are generally a few inches thick, and a foot or a few feet long. These contain quartz, plagioclase, garnet, epidote, zoisite. There appears to be a B.I.F. horizon

near the top of this formation in the southern part of New Broken Hill Consolidated Limited. Thickness of Formation No. 4 is generally 300 to 400 feet, but it appears to become very thin in the eastern syncline, underneath the ore bodies.

No. 5.—"Potosi" gneiss. The rock is actually a quartz-felspar (plagioclase and orthoclase)-garnet-biotite gneiss tending to granulite in places. This is the main horizon of the "Potosi Gneiss" (and granulite) and "Footwall Gneiss" of E. C. Andrews' maps (1), and the "Potosi-Footwall Gneiss" (XII Formation) of Gustafson et al. (6). The "Potosi Gneiss" and "Potosi-Footwall Gneiss," however, also included some granulite on the western side of the lead lode ore bodies in North Broken Hill Limited, this now being recognized as a higher stratigraphic horizon. (It actually falls in Formation No. 8.) The thickness of Formation No. 5 is variable. For example, on Section No. 30 (although exact estimation is difficult because of folding) it varies from a few hundred feet thick at the surface, to only a foot or two at No. 21 Level.

No. 6.—Sillimanite-sericite-garnet-biotite gneiss with some siliceous layers, and calc-silicate ellipsoids. In the underwall of the ore bodies in The Zinc Corporation Limited and New Broken Hill Consolidated Limited the gneiss is fairly fine grained and well bedded. Thickness is generally 50 to 200 feet.

No. 7.—In this formation have been placed the lead lode ore bodies (Nos. 2 and 3 lenses) and separating rock. It also includes the weak lode developments which are the stratigraphic extensions and equivalents of the lead lode ore bodies. Where recognizable these usually consist of garnet quartzite or siliceous gneiss with blue quartz, pyrrhotite (core rusts on long exposure to the atmosphere), and traces of green felspar, galena, sphalerite and chalcopyrite. This formation can be divided into—

No. 7 (a).—No. 3 lens ore formation. In the northern half of The Zinc Corporation Limited this has a quartz-fluorite gangue, becoming calcitic and rhodonitic in the southern part. Passing south into New Broken Hill Consolidated Limited it diminishes in size, becomes more calcitic, and eventually merges with No. 2 lens. At Section No. 62 (Fig. 3) it can no longer be recognized as a separate formation. Typical grade of No. 3 lens ore mined in The Zinc Corporation Limited is 11% Pb, 8 ounces silver per ton, 14% Zn.

No. 7 (b).—Separating rock between Nos. 2 and 3 lenses. In most of The Zinc Corporation Limited ground it consists of garnet-sillimanite gneiss and quartzite, and may be 50 to nearly 100 feet thick. Southwards it passes into garnet quartzite, carries appreciable galena in New Broken Hill Consolidated Limited, and finally lenses out completely.

No. 7 (c).—No. 2 lens ore formation. This has a fairly consistent calcite-rhodonite gangue. Typical grade of No. 2 lens ore produced in both mines is 12% Pb, 3 ounces silver per ton, 10% Zn.

The thickness of Formation No. 7 is very variable. In the ore-bearing zone in The Zinc Corporation Limited and New Broken Hill Consolidated Limited the formation probably averages over 100 feet thick. Where it is represented only by quartzitic beds, it may be as little as a few feet thick.

No. 8.—Quartzite and garnet-biotite-sillimanite gneiss, with some lead-zinc bearing layers. This is the rock separating the lead lode and zinc lode formations. It contains No. 1 lens ore formation (the overwall zinc lode of Gustafson (4)) in The Zinc Corporation Limited and New Broken Hill Consolidated Limited. No. 1 lens ore formation typically consists of an upper and a lower layer, and these become particularly well developed in New Broken Hill Consolidated Limited (Fig. 3). Gangue is predominantly quartz, and grade of No. 1 lens ore produced averages 9% Pb, 1 ounce silver per ton, 15% Zn. Formation No. 8 also contains a discontinuous band of "Potosi" gneiss in places, especially in North Broken Hill Limited. Formation No. 8 probably averages 100 to 150 feet thick.

No. 9.—This includes the zinc lode ore bodies and separating rock. As with the lead lode formation (No. 7) the stratigraphic equivalents of the zinc lode ore zone are widespread as garnet quartzite and feebly mineralized gneiss (sphalerite almost invariably being in excess of galena). In The Zinc Corporation Limited and New Broken Hill Consolidated Limited mines, Formation No. 9 is a predominantly siliceous zone averaging 150 feet thick, but being much thicker in places. The formation is almost continuously mineralized from bottom to top, but within it there are a number of well defined layers in which the mineralization reaches ore grade. The most important of these layers are termed A lode and B lode.

A Lode—this was previously known as the rhodonitic zinc lode. Principal gangue minerals are quartz, manganese garnet, and rhodonite. It occupies the stratigraphically lowest portion of Formation No. 9, and is itself in places divisible into an upper and a lower layer separated by mineralized garnet quartzite. Grade of ore from the better portions of A lode averages 4% Pb, 1 ounce silver per ton, 13% Zn.

B Lode—this is the lowermost layer of what was previously known as the siliceous zinc lode. It lies, on an average, about 40 feet stratigraphically above A lode. Principal gangue minerals are quartz and felspar. Typical grade of B lode ore mined is 5% Pb, 1 ounce silver per ton, 18% Zn. Above B lode there is a zone of variable but generally weak zinc-lead mineralization that constitutes the rest of what was previously known as the siliceous zinc lode.

The segregation of the ore-bearing horizons into formations is somewhat arbitrary. The treatment presented here is different from that of Gustafson et al. (6) who placed greater emphasis on Nos. 2 and 3 lenses as individual formations, since they were known throughout the length of the mining area. The present segregation has been influenced by the greater amount of exploratory and development information now available, especially in The Zinc Corporation Limited and New Broken Hill Consolidated Limited mines. Away from economic ore, Nos. 2 and 3 lenses cannot be distinguished as such, but the lead lode zone can often be distinguished from the zinc lode zone, so it seems logical to class each of these as formations, and the individual ore lenses within them as subdivisions of these formations. The

No. 1 lens group ore bodies fall naturally into Formation No. 8 between the lead lode and zinc lode formations.

No. 10.—Sillimanite-garnet-biotite gneiss (generally fairly siliceous) with layers of quartzite. In the southern part of New Broken Hill Consolidated Limited the formation appears to become predominantly quartzitic. In this area also there is at least one lenticular bed of "Potosi" gneiss. Thickness of Formation No. 10 is generally 300 to 600 feet in the two mines.

No. 11.—The upper amphibolite. Macroscopically this appears to be very similar to the amphibolites in Formations Nos. 2 and 3. Surface exposures and diamond drill core show the upper amphibolite to consist of a number of adjacent bands and lenses making up a formation which is generally between 50 and 100 feet thick.

No. 12.—Sillimanite-garnet-biotite gneiss with quartzitic layers. This formation is similar to Formation No. 10. Thickness is generally 300 to 400 feet.

No. 13.—The upper granitic gneiss. There seems to be no constant macroscopic difference between this and the lower granitic gneiss. In the southern part of the field, this is the uppermost formation revealed in the Hanging Wall Basin, and here Formation No. 13 may be 1,000 feet thick.

Thickness of the Sequence

Estimates of the thickness of the sequence, and of the individual formations, are subject to considerable uncertainty because of variation from section to section, and because it is difficult to know how much allowance to make for folding in estimating true stratigraphic thickness. In the mining area of The Zinc Corporation Limited and New Broken Hill Consolidated Limited (i.e. in the eastern limb of the Hanging Wall Basin) the granitic gneisses are mostly 3,000 to 3,500 feet apart (Fig. 1). This is greater than the true stratigraphic thickness, which might be 2,000 to 2,500 feet (with the rocks in their present highly metamorphosed condition).

In the western limb of the Hanging Wall Basin we can recognize Formations No. 5 to No. 12 below the upper granitic gneiss. The distinctive formations below No. 5 either lens out or fold over into an anticline before reaching the surface. Formations No. 5 to No. 12 are much thinner (by a factor of about two) in the western limb of the Hanging Wall Basin than in the eastern limb (Fig. 1).

The known ore bodies are confined to Formations No. 7, No. 8 and No. 9, and occur in a stratigraphic thickness averaging 300 to 400 feet, which in The Zinc Corporation Limited and New Broken Hill Consolidated Limited lies approximately in the middle of the Mine Sequence outlined above.

THE STRUCTURAL INTERPRETATION

General.—In the vicinity of The Zinc Corporation Limited and New Broken Hill Consolidated Limited leases there are three named fold structures.

1. The Hanging Wall Basin, which is a major synclinal structure.
2. The Lode Structure, which is a drag fold consisting of an anticline (Western Anticline) and a syncline (Eastern Syncline). It is to this structure, which is situated on the steeply dipping east limb of the Hanging Wall Basin, that the various ore layers owe their folded character.
3. The Foot Wall Structure, which is a drag fold consisting of the Foot Wall Anticline and the Foot Wall Syncline. This drag fold is situated on the east limb of the Hanging Wall Basin to the east of the Lode Structure.

Evolution of the Present Structural Interpretation.—Figure 2 depicts the 1950 interpretation of Gustafson et al. (6). In this, the overall structure was regarded as anticlinal, and the distinctive stratigraphic units such as the granitic gneiss, amphibolite and "Potosi Gneiss" were thought to be unique. The ore bodies were thought to occupy the "main shear" and folds on the western side of the "main shear." It was deduced that the main mass of "Potosi-Footwall Gneiss" on the eastern side of the ore bodies was synclinal in form, which made the "Alma Anticline," further to the east, a structural necessity if the overall structure were to be anticlinal. If marker horizons were absent from places where the interpretation required them to be, they were thought to have been sheared out by attenuation on the limbs of folds.*

This interpretation fitted the information available to the Central Geological Survey very well. It was influenced not only by the occurrence of similar looking granitic gneiss and amphibolite on both sides of the structure, but also by the occurrence of prominent "Potosi Gneiss" on the western side of the ore bodies at North Broken Hill Limited, as evidenced by the following statement in Gustafson's 1939 report (4, II, p. 55): "The correlation of the Footwall Gneiss with the Potosi Gneiss as a single stratigraphic horizon has much to recommend it. The lode horizons definitely underlie the Potosi Gneiss in the Western Anticline at the North Mine." The lead lode ore bodies (i.e. Nos. 2 and 3 lenses) do in fact underlie this horizon of "Potosi" gneiss, but this in turn is overlain by the zinc lode zone, and is a separate horizon from the main "Potosi" gneiss (Formation No. 5) to the east of the lead lode.

This 1939 version of the structure was first questioned in 1947 by Gustafson and King when it was realized that the interpretation of the form of the zinc lodes had to be altered—in fact back to the essentials of Burrell's 1936 interpretation. The 1939 concept of the "main shear" in The Zinc Corporation Limited and Broken Hill South Limited was a plane of attenuation along the eastern side of the main Nos. 2 and 3 lens anticlines. It was also realized in 1947 that the upper part of the "main shear ore" was actually the eastern limb of No. 2 lens. Mapping by a Zinc Corporation geologist (W. N. Thomas) in Broken Hill South Limited in 1950–51 established the existence of the Eastern Syncline, by showing that the No. 3 lens horizon was going

* It is interesting to note that we now prefer to think of discontinuities in beds being the result of sedimentary lensing rather than shearing out.

upward on the eastern side of the No. 2 lens "main shear ore," instead of downward into the "Footwall Basin" as postulated by Gustafson. The understanding of the structure of the ore bodies reached by 1951 is essentially the same as that accepted and used by the geologists of The Zinc Corporation Limited and New Broken Hill Consolidated Limited at the present time.

The 1939 interpretation was further weakened by the results of drilling to the east of and beneath the ore bodies in the The Zinc Corporation Limited. In 1948 diamond drill holes 631 and 653 were drilled east on Section No. 30 (Fig. 1) to test the postulate of the favorable horizons in the Alma Anticline, but the results gave no support for the existence of this structure. Holes drilled in the underwall of the ore bodies intersected "Potosi" gneiss, amphibolite and bedded iron formation in positions where these should not occur according to the 1939 interpretation. Similar information was found when the cores of some old holes drilled in the central part of the field in 1940 were rediscovered. The results from these holes show that the whole sequence in the ore environment has tops facing west.

The Hanging Wall Basin.—The main evidence for the existence of this fold lies in the fact that a central core of granitic gneiss (Formation No. 13) is flanked to the east by the steeply dipping Mine Sequence, which has tops facing west, and to the west by a sequence of beds that has strong similarities with the portion of the Mine Sequence from Formation No. 5 to Formation No. 13. Cleavage-bedding relationships also indicate that the beds on the western side have tops facing east. To the north of The Zinc Corporation Limited leases the evidence has been supported by diamond drilling.

The Lode Structure.—By reason of the presence of ore in this structure it is the best known fold system in the Broken Hill field. Broadly speaking, a large drag fold, the principal components of which are the Eastern Syncline and the Western Anticline (see Fig. 3), has been impressed upon all of the conformable ore layers.

Detailed information collected during the course of testing and extraction of ore has shown the Eastern Syncline and Western Anticline to be far from simple structures. In detail it is found that the principal components of the ore-bearing structure are made up of a series of lesser folds which develop in an en echelon pattern sub-parallel to the general axial trend of the major components. In The Zinc Corporation Limited leases the lesser folds appear to be arranged in a right hand pattern. However in the southern portions of the New Broken Hill Consolidated Limited mining area folding of the "B" Lode formation shows a strong left hand arrangement of the en echelon folds. Thus although the form of an overall drag fold persists through the two mines, individual lesser folds are not continuously traceable. These lesser folds were recognized by Gustafson (4). For some of the minor folds that did not seem to fit the major fold pattern a second period of folding was postulated. The present interpretation regards both the overall drag fold and its components as representing the deformational response to stress couples rather than to pure compressive forces.

At the northern boundary of The Zinc Corporation Limited leases the

Lode Structure plunges at a steep angle to the south. At this point the major developments of ore are in the No. 2 and No. 3 lenses with the zinc lodes only weakly developed. Ore in the No. 2 and No. 3 lenses extends from near surface to a vertical depth of 2,100 feet with a maximum folded width of 200 feet. The large vertical extent of ore results from the development of No. 2 lens in the attenuated east limb, and in the deep, tight, isoclinal keel of the Eastern Syncline. The steeply dipping axial plane of the Western Anticline at this point is approximately 100 feet west of the axial plane of the Eastern Syncline.

The plunge of the ore-bearing structure flattens to an average of 30° south in the central and southern portions of The Zinc Corporation Limited and, still further south in New Broken Hill Consolidated Limited, there is further flattening to an average of 5° south in the vicinity of Section No. 62 (see Figure 3). The average plunge angles refer to the overall plunge of the orebodies. However, the very nature of the en echelon development of lesser folds produces many localized reversals and irregularities of plunge. In addition to the general flattening of plunge south of The Zinc Corporation Limited northern boundary the Eastern Syncline and Western Anticline become more open structures to the south, resulting in minable ore widths of over 500 feet.

Not only do the orebodies show marked changes in cross sectional outline along strike, but also the distribution of ore in the drag fold structure is variable. The proportions of ore in the synclinal, anticlinal and limb positions show considerable changes between various cross sections.

In their 1953 publication, King and Thomson (8) first questioned the late stage emplacement of the sulfides, and suggested that the mineralization existed in the beds before folding and metamorphism. Now, rather than thinking that ore concentration is controlled by structure it is considered that physical characteristics of the ore layers played a large part in determining the fold response to given stress couples. This concept also suggests that the fold shapes and variations in thickness observed in the various metamorphosed beds, including the ore layers, are not all due to tectonic forces. Slump structures and variations in thickness of the original sediments, although modified by later folding, are considered to have played an important part in the geological picture as seen now.

The Foot Wall Structure.—The principal components of this structure are the Foot Wall Anticline and the Foot Wall Syncline. These folds lie to the east of the Lode Structure and are most clearly defined by the outline of the main "Potosi" gneiss (Formation No. 5) as defined by underground diamond drilling and development. There is considerable apparent thickening of this formation where it is involved in the Foot Wall Structure. It is suggested that not all of this thickening is due to tectonic folding. In fact the fold itself may have been initiated by a subsiding basin that locally collected greater thickness of sediment, which on metamorphism produced the "Potosi" gneiss.

Deep diamond drilling from underground openings has shown lower

horizons such as the main lower amphibolite (Formation No. 3), the bedded iron formation (in Formation No. 2) and the lower granitic gneiss (Formation No. 1) to be involved in both the Foot Wall and the Lode Structures (see Figure 1).

Faulting.—Numerous faults of small displacement have been intersected in the mine workings of the two mines. However none has seriously interrupted the continuity of ore, and only one, a steep, north dipping, east–west striking rupture between the No. 15 and No. 16 Levels in The Zinc Corporation Limited, has a measured displacement approaching 100 feet.

A zone of shearing, referred to as the "Main Shear" by Gustafson et al. (6) is associated with the eastern margin of No. 2 Lens ore in the attenuated east limb of the Eastern Syncline. This zone of shearing, which, in the upper portions of the mines is essentially coincident with the bedding direction, is found at lower levels to dip west and away from the bedding direction through the limbs of the eastern syncline and in the deepest mine levels at New Broken Hill Consolidated Limited is almost coincident with the axial plane of the Western Anticline.

Where the shear parallels bedding it is represented by a relatively narrow band of schist. Where bedding is transgressed it broadens into a zone of brecciation up to 100 feet in width. Individual fracture planes within the zone show displacements of a few feet but the zone as a whole does not produce any significant displacement.

ACKNOWLEDGMENTS

This paper presents the results of the work of numerous mine and field geologists, whose efforts over a period of many years have given us our present understanding of the geology of the Broken Hill deposit. These efforts are gratefully acknowledged. The more important individual contributions have been mentioned in the text.

Special thanks are due to Mr. Haddon F. King, Director of Exploration of Consolidated Zinc Proprietary Limited, for first suggesting that the paper should be written, and for his constructive criticism of the preliminary drafts. B. J. Drew and J. B. McManus also assisted by checking the drafts.

Finally the authors wish to thank the managements of The Zinc Corporation Limited and New Broken Hill Consolidated Limited for permission to publish the material here presented.

BROKEN HILL,
NEW SOUTH WALES,
AUSTRALIA,
May 8, 1961

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THE IRON ORE DEPOSITS OF EL-BAHARIYA OASIS, EGYPT

F. M. NAKHLA

ABSTRACT

The iron ore deposits occurring at Gebel Ghorabi, in the northern part of El-Bahariya Oasis, consist of four different types of ore. The chief ore minerals are goethite, hematite, and other hydrated forms of iron oxides together with a small amount of pyrolusite, psilomelane, and manganite. Quartz, calcite, halite, and clayey material are the prevailing gangue minerals.

The detailed study of polished and thin sections of the various types of ore specimens, particularly the interpretation of mutual relationship between the constituent minerals, has aided the determination of the paragenesis, and in revealing the probable mode of formation of the iron ore deposits. It was concluded that these iron ores are probably epigenetic deposits, that have been formed by metasomatic replacement of Lower Eocene limestone as previously advocated by Gheith, as well as by precipitation from colloidal solutions, and by cavity fillings.

INTRODUCTION

In Egypt the iron mineralization is widely distributed. The most important occurrences of Egyptian iron ore deposits are shown in Figure 1, and include east of Aswan, several localities in the Eastern Desert, and El-Bahariya Oasis. The iron ore deposits at Gebel Ghorabi, in the northern part of El-Bahariya Oasis, were previously studied by Ball and Beadnell (3), Afia and Nessim (1), Faris et al. (4), and Gheith (5). According to Faris et al. (4) the stratigraphic sequence of the formations in El-Bahariya Oasis can be schematically represented by Figure 2. Gebel Ghorabi, where the iron ore deposits are localized, consists of sandstones, sandy shales, and clays of Cenomanian age, overlain by conglomerates and limestones of Lower Eocene. The iron ore deposits, which mainly occur in the Lower Eocene limestone, are in the form of beds extremely irregular in shape and extension, with great variation in thickness and composition. According to Gheith (5) the ore is essentially composed of goethite with a little magnetite, pyrolusite, and halite though many samples consist mainly of siderite or hematite. Hume (6) and others estimated the proved reserves of the ore to be about 22 million tons of relatively high- to medium-grade ore.

Ball and Beadnell (3), Hume (6), and Attia (2) considered these deposits to be of sedimentary origin, being formed by precipitation from solutions under shallow lacustrine conditions. Gheith (5) advocated their formation by metasomatic replacement of limestones, as evidenced by field observations, and by the occurrence of few pockets of ore containing Nummulites atacicus and Nummulites subatacicus that were completely replaced

by goethite and siderite, and thus excluded the possibility of its formation as a shallow water lacustrine sediment.

This work, which has been carried out in the National Research Centre, Cairo, includes the results of the examination of polished and thin sections of the iron ore deposits of El-Bahariya Oasis, and by a few chemical and spectrographic analyses. This study has proven to be of great help in determining the paragenesis, and in suggesting the probable mode of formation of the iron ore deposits of El-Bahariya Oasis.

MINERALOGY OF THE ORES

A cursory examination of the iron ore specimens shows that there are four distinct types of ore, which vary to a great extent in form, texture, porosity, specific gravity, mineralogical constitution, and chemical composition. A brief description of these types is given here.

The first type of ore is the most common, and is characterized by light to dark brown color, dull to resinous lustre, and a pisolitic to oolitic texture in which the kernels range from 2 to 5 mm in diameter. The ore consists of an intimate mixture of goethite and hematite with a siliceous matrix, which gives the ore increased hardness. The chemical analysis of this type of ore follows: Fe = 30.5%, Mn = 4.0%, CaO = 2.66%, MgO = 0.75%, and SiO_2 = 38.82%.

The second type of ore is less common, but its grade and specific gravity are higher than those of the preceding type. The ore is vesicular, brownish

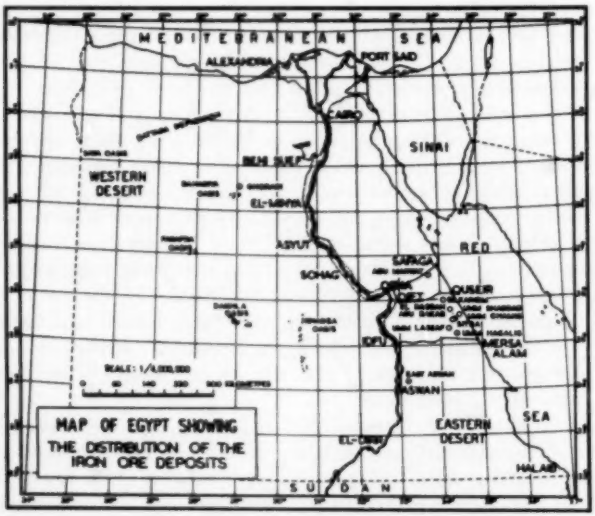

FIG. 1. Map showing the distribution of the iron ore deposits in Egypt. (After A. Sabet.)

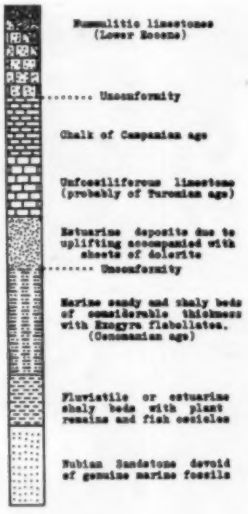

FIG. 2. Schematic columnar section showing the succession of beds in El-Bahariya Oasis.

black in color, with submetallic lustre, and is mainly composed of an intimate association of hematite, pyrolusite, and psilomelane. The manganese oxides in places form patchy irregular aggregates surrounded with hematite. Some specimens of this type of ore contain remains of broken shells of lamellibranchs and inner casts of gastropods, which are completely replaced by iron and manganese minerals. The chemical composition of this kind of ore is: Fe = 51.5%, Mn = 7.5%, and SiO_2 = 0.4%.

The third type is a hard ore characterized by a dark brown color, submetallic lustre, and is essentially composed of goethite, hematite, together with a small amount of pyrolusite. The iron content in this ore is about 45.3 percent, but the manganese constitutes only about one percent of the ore. Quartz and calcite are the dominant gangue minerals.

The fourth type is a relatively low-grade ore in which the iron content is about 25.5 percent, and silica forms about 60 percent. This ore has a yellowish color, resinous lustre, and is composed essentially of limonitic material mingled with quartz and calcite. The calcite fills or lines small irregular cavities scattered in the massive ore.

Spectrographic analysis showed that the four types of ore generally contain the same minor and trace elements, which are:

(a) Major constituents (more than 2%) include iron, silicon, manganese, sodium, and calcium.

(b) Minor constituents (more than 0.01%) include aluminum, and magnesium. Phosphorus and sulfur are also minor constituents in the ore.

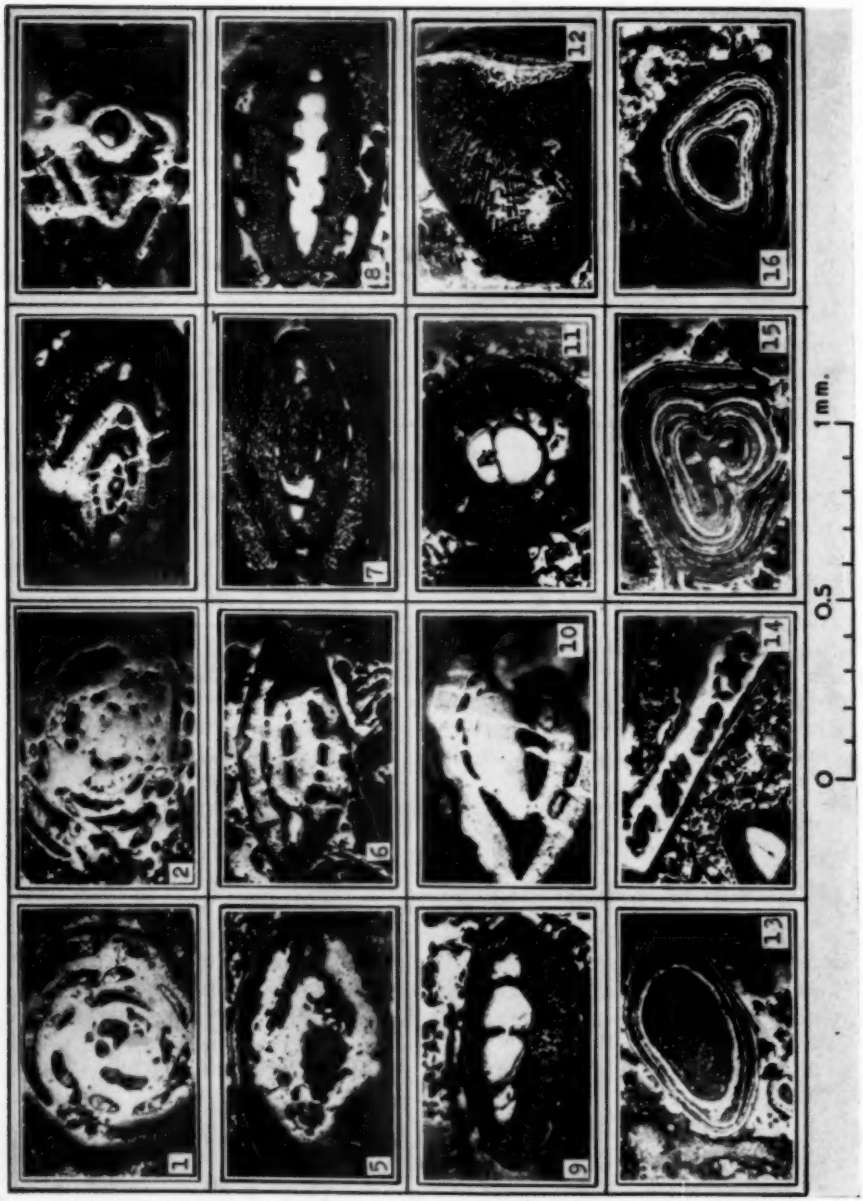

FIG. 3.

(c) Traces (less than 0.01%) include barium, copper, chromium, and titanium.

Mineralographic examination of the polished sections of some specimens of the first type of ore reveals interesting information regarding its composition and texture. Such investigation shows that the ore is composed essentially of goethite replacing, to varying degrees, the calcareous matter including micro as well as macro fossils. In some sections it was observed that the original internal structure of the replaced shells had been partially preserved, though complete replacement is commonly accompanied with the obliteration of the internal structure of the shells. Some polished sections were kindly investigated by M. A. Ghorab,[1] who determined the following microfossils:

(1) Alveolina species.
(2) Assilina species.
(3) Nummulites atacicus.
(4) Nummulites deserti.
(5) Nummulites subatacicus.
(6) Operculina lybica.

Besides the above mentioned microfossils, all the examined polished sections contain fragments of lamellibranchs, fish teeth, bone fragments, and other remains that were difficult to identify owing to their poor state of preservation due to mineralization. The determined fauna indicate beyond doubt that the replaced rock is of Lower Tertiary age, most probably belonging to the Ypresian period. Therefore, it is clearly evident that the iron ores of El-Bahariya Oasis have been formed by the metasomatic replacement of biochemical limestone. This conclusion is in perfect agreement with the idea previously suggested by Gheith (5) in 1955. However, most of the polished ore specimens, examined by the author, showed that the goethite commonly exhibits colloform texture, which is usually considered as a criterion of precipitation from colloidal solutions. Moreover, in many thin and polished sections of the oolitic or pisolitic ore it has been observed that quartz and goethite fill the primary openings and the interstitial spaces between the replaced calcareous shells. Examination of thin sections revealed that large and subhedral crystals of quartz occupy the open spaces enclosed within the replaced shells. Pyrolusite, psilomelane, and probably manganite occur in small quantities and it seems that the manganese minerals

FIG. 3. 1, 2. Photomicrographs of a polished section showing Alveolina species partially replaced by goethite (white). 3, 4, 5. Photomicrographs of a polished section showing different stages of the replacement of Nummulites subatacicus by goethite. 6. Photomicrograph of a polished section showing Nummulites deserti almost replaced by goethite. 7, 8, 9, 10. Photomicrographs of a polished section showing Nummulites species gradually replaced by goethite. 11. Photomicrograph of a polished section illustrating the filling of the core of a Nummulite shell by goethite. 12, 13. Photomicrographs of a polished section showing the partial replacement of the shells of lamellibranchs by goethite. 14. Photomicrograph of a polished section illustrating an unidentified object almost replaced by goethite. 15, 16. Photomicrographs of a polished section illustrating colloform texture commonly exhibited by goethite probably due to precipitation from colloidal solutions.

[1] Chief Paleontologist of the Anglo-Egyptian Oilfields Company Limited, Egypt.

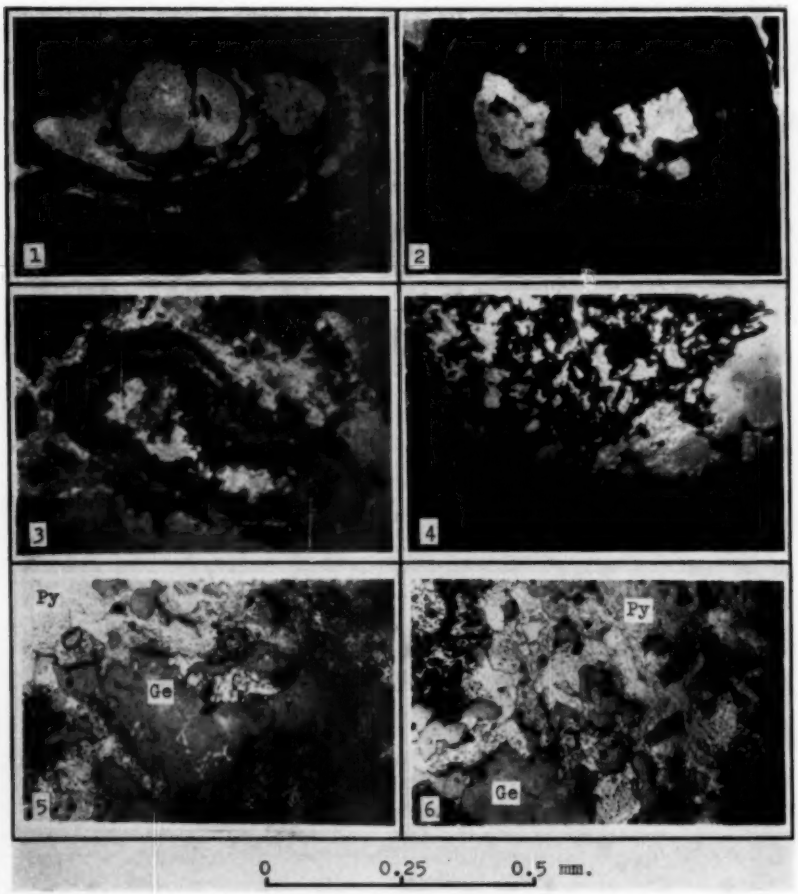

FIG. 4. 1. Photomicrograph of thin section showing interlocking crystals of quartz (white) filling primary pores in a shell of Nummulites species, while the calcareous matter has been replaced by hydrated iron oxides (black). 2. Photomicrograph of a thin section showing subhedral crystals of quartz enclosed within a Nummulites shell completely replaced by goethite (black). 3. Photomicrograph of a thin section showing cavity fillings of quartz (white) in the center of a shell that shows banded replacement by iron oxides (black and dark grey) along the margin. 4. Photomicrograph of a thin section showing remnants of calcite (white) enclosed within pyrolusite (black), which is selectively replacing the calcite (×-nicols). 5. Photomicrograph of a polished section showing an early stage of the replacement of goethite (Ge) by pyrolusite (Py). 6. Photomicrograph of a polished section showing an advanced stage of the replacement of goethite (Ge) by pyrolusite (Py).

crystallized at a later stage after the precipitation of goethite. Figure 1 illustrates the different stages of replacement and the colloform texture commonly exhibited by goethite in the oolitic or pisolitic type of ore.

Polished sections of the second type of ore show that it is composed essentially of an intimate mixture of hematite and pyrolusite. The pyrolusite forms aggregates of tiny interlocking needle-like crystals that show high reflectivity and moderate anisotropism. Examination of the polished and thin sections of the third type of ore shows that it is mainly composed of goethite and hematite, together with a small amount of pyrolusite. The pyrolusite replaces selectively the calcite leaving islets of the latter amidst the iron and manganese minerals. Thin sections of the fourth type of ore shows that it consists mainly of quartz and calcite impregnated with hydrated iron oxides, hematite, and manganese oxides. Figure 2 illustrates photomicrographs of some polished and thin sections of certain ore specimens from the iron ore deposits of El-Bahariya Oasis.

PARAGENESIS

The nature of the ore minerals that constitute the iron ores of El-Bahariya Oasis and their textural relationship throws light upon the paragenesis and the probable mode of formation of these deposits. From the present study the following conclusions have been drawn:

(1) The metasomatic replacement of the biochemical or autochthonous limestone by goethite and pyrolusite is a conspicuous feature in the oolitic or pisolitic type of ore.

(2) The goethite commonly exhibits colloform texture indicating that it was most probably precipitated from a colloidal state.

(3) The common presence of cavity fillings of quartz, goethite, and calcite in many of the polished and thin sections of the various types of ore.

All the above mentioned facts suggest that the processes of metasomatic replacement, precipitation from colloidal solutions, cavity filling in open spaces, and impregnation have contributed, to various degrees, in the formation of the iron ore deposits. It is not necessary to assume that all these processes were operating at the same time during the mineralization period, since the relative concentration of the various metals, the pH value of the solutions, the temperature gradient, and the original composition and texture of the replaced rocks are important factors in controlling the mode and order of precipitation of silica, iron, and manganese from mineralizing solutions. Consequently, it is evident that the sedimentary origin, by precipitation from solutions under shallow lacustrine environment, ascribed to the iron ore deposits of El-Bahariya Oasis by Ball and Beadnell (3), Hume (6), and lately by Attia (2) is unacceptable in the light of the previous work carried out by Gheith (5) in 1955, and of the present study. The author is inclined to believe that the mineralization started after the Tertiary tectonics which, according to Ibrahim (7), played an important role in the formation of the Lybian Desert depressions, including El-Bahariya Oasis itself. It is most probable that the mineralization started in post-Eocene or Miocene times, and

is related to basic activity resulting from Tertiary basalts. Although field observations do not give conclusive evidence of an epigenetic or syngenetic origin for the iron ore deposits of El-Bahariya Oasis, yet it seems that the Tertiary tectonics has led to the rise and migration of basaltic magma, along abyssal fissures, towards the surface, and in the meantime has furnished the necessary channels for the ascending mineralizing solutions. Furthermore, it appears that the hydrothermal solutions, which are genetically related to the Tertiary volcanism, have partially contributed but mainly have mobilized and leached several elements, including silica, iron and manganese from other source rocks. The ore-bearing solutions, during their migration upwards, have circulated through favorable channels until they came into contact with the Lower Eocene limestone, where the conditions had been most favorable for metasomatic replacement, and for precipitation from solutions. Recently, Kennedy (8), Morey and Hesselgesser (11), Morey (10), and White (13) have shown that enormous quantities of silica, sodium chloride, and other salts could be transported in solution particularly in the dense vapor phase that is often associated with volcanic activity. The fact that the basal Eocene conglomerates in Gebel Ghorabi, where the iron ore deposits are mainly localized, are in certain parts totally permeated and replaced by iron minerals (5) may indicate that the iron ores of El-Bahariya Oasis are most probably epigenetic deposits, the localization of which had been favored by the metasomatic replacement of Lower Eocene limestones overlying the basal conglomerates. Ljunggren (9) has also shown that the bog iron and manganese ores, particularly those of recent age, possess a great adsorptive power and are characterized by the presence of traces of a large number of elements including K, Rb, Cs, Sr, Ba, Ni, Co, Pb, B, Be, V, Cr, and Mo. Such an association of trace elements is not present in the iron ores of El-Bahariya Oasis indicating that a sedimentary origin, by precipitation in bogs under lacustrine conditions, is a rather remote probability. The activated silica has probably crystallized at an earlier stage in the primary openings found in the limestone, which was later replaced by iron and manganese minerals. Pyrolusite seems to have crystallized after the precipitation of iron or most probably overlapped it. The sequence of deposition of the constituent minerals of the iron ores of El-Bahariya Oasis, i.e., the paragenesis, seems to be as follows: quartz, goethite, hematite, pyrolusite, psilomelane, and calcite.

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PUMICE AND PERLITE IN A RHYOLITE COMPLEX IN HUNGARY

ERVIN G. OTVOS, JR.

ABSTRACT

The plagioclase rhyolite complex of the Kishegy Hill in the Mátra Mountains, northern Hungary, has been quarried for its economic materials since the Middle Ages. It contains the following textural rhyolite types: pumaceous, perlitic, spherulitic, lithophysae and felsitic rhyolite. The pumice and perlite, at the bottom of the complex are the most water-rich. The spherulitic types show an increasing amount of strained crystallization and a decreasing amount of glassy groundmass and water-content. The lithophysae and felsitic types, forming the upper part of the complex, are completely crystallized. The water content of each type has characteristic averages, but no distinct boundaries of their minimum-maximum range. The water in the glassy groundmass of the vitric varieties is mechanically enclosed. In the lower levels of the complex the different rhyolite types vary characteristically. These properties reflect the inhomogenous physical conditions of the original lava.

The water of the rhyolite varieties may have been derived both from deep magmatic zones and from surface rocks, as well as from ponded surface water. Extensive investigations and analyses indicate that the development of the various types is due to the different physical conditions in the lava. With the exception of the water-content, no chemical differences could be ascertained among the varieties, including the ferri: ferro-oxide ratios of the vitric types. The origin of the various colors of the vitric and crystalline rhyolite types is thought to depend upon the speed of crystallization and the Fe_2O_3-content.

INTRODUCTION

On the south rim of the Mátra Mountains of northern Hungary is an isolated plagioclase rhyolite complex on the hill of Kishegy. Its formation is connected with the great Miocene (Helvetian-Tortonian) volcanism of the Mátra Mountains, which formed mainly andesites and rhyolite tuffs. The hill of Kishegy is situated 4 km north of the town of Gyöngyös. The rhyolite complex constitutes the upper part of this 388 m hill. The approximate maximum dimensions of the complex are: length 1,400 m, width 500 m, thickness 90 m. It lies on a stratified, decomposed, montmorillonized pyroxene andesite tuff, which is underlain by similarly decomposed pyroxene andesite. The base of the rhyolite complex dips SW over a vertical distance of 100 m.

The first up-to-date, detailed account of the rhyolite was given by Mauritz (6), who described a vitric rhyolite type, overlain by a felsitic type, as well as a spherulitic variety. Varju (14, 15) described in ascending order the succession of the rhyolite types on Kishegy as: pumaceous, perlitic, spherulitic,

polyedrical spherulitic,* lithophysae and lithoidal rhyolite. The present paper attempts to clarify some points of the conditions of the formation of the Kishegy rhyolite types. Chemical, mineralogical and geological methods were employed. The investigations were carried out in the following institutions:

a) Chemical analyses (49 complete, 22 partial): Central Laboratory of the Mineral Mining Industry (Dr. Z. Juhász), State Geological Institute—Chemical Department (V. Tolnay—Mrs. L. Nemes), Laboratory of Mátra Mineral Mines Company (J. Lukács).
b) Thermal analyses: Technical University of Budapest—Institute of General Chemistry 8 derivatograph analyses (S. Gál—Gy. Liptay), Chemical University of Veszprém, Department of Mineralogy 7 DTA, DTG, TG-analyses (Dr. E. Nemecz—Á. Pünkösti).
c) Accessory and trace element analyses (17 quartz spectrographic analyses): University of Science, Budapest—Department of Mineralogy-Petrology (Dr. I. Kubovics).
d) X-ray investigations (8 analyses): Technical University of Construction and Communication, Budapest—Mineralogical-Geological Department (T. Mándy), Chemical University of Veszprém—Department of Mineralogy (Dr. E. Nemecz—Á. Pünkösti), Institute of Metallurgical Research—X-Ray Department (Dr. T. Kotsis).

MINERALOGIC AND PETROGRAPHIC DESCRIPTIONS

Mauritz (6) has given an excellent description of the constituent minerals in the whole complex. Porphyritic minerals are twin-plated plagioclase-feldspars (andesine-labradorite with oligoclase rim) and biotite; both attain 2 mm. The recognizable microlites consist of the above minerals and some magnetite and zircon. The index of refraction for the glassy groundmass was given as 1.5. During the present investigations sanidines were also found among the porphyritic minerals (Dr. J. Kiss) and the X-ray analyses reveal quartz and crystobalite in the perlite and in the felsitic rhyolite. The latter minerals must be present as microlites, as they were not recognized under the microscope.

VARIETIES AND THEIR DISTRIBUTION

Pumice.—Most of its volume is composed of glassy and porous groundmass, containing embedded porphyritic and microlitic crystals. The rock is light gray in color with a silky lustre and flow structure; specific gravity is 1.9. The pumice occurs on the east and south part of the hill, and its greatest thickness of at least 27 m is in the lower prospecting shaft. The base of the pumice is not exposed, but it certainly overlies the andesite tuff. The roof, exposed on the southern slope is spherulitic and polyedrical spherulitic rhyolite. Perlitic nests and bands occur commonly in the pumice of the southern slope.

* "Mieuitic."

Perlite.—The perlite is medium gray in color or in some places deeper gray, pitch-black, or dense with a vitreous lustre and shelly fracture; its specific gravity is 2.3. The glassy, X-ray amorphous groundmass shows few perlitic cracks and some microlites. In the large southwestern quarry it immediately overlies the andesite tuff along a 100 to 120 m section. Here the thickness of the perlite varies from 1 to 3 m. Perlite is also found in other vitric rhyolite types; in the pumice the perlite bands have a maximum extension of 50–60 cm. On the southeastern and southwestern parts of the hill a transitional perlite-pumice variety is exposed. The pumice and perlite in Kishegy are considered by the author to be genetically strongly associated.

Spherulitic Rhyolite Types.—These are generally light to medium gray, lustreless rocks. The diameter of the spherulite globules may reach several millimeters. Under the microscope, the spherulites are gray or yellowish brown, and show a radiating, skeleton crystalline structure. Mauritz (6) has described the rare nonhomogeneous structure of the spherulites, their weak birefringence and positive optical character, as well as the amoeboid brown coloring that may enclose a part of the spherulites. Most of the spherulites are rounded and homogenous, but spherulites consisting of 2 to 3 concentric girdles of different (yellow-brown) colors and a fringed outer rim, composed of half-moon shaped, petallike forms are not rare. Their shape may also be irregularly elongated or resemble an oval cockade. The concentric rings and ovals point to the interruptions in the growth. The spherulites may also parallel the flow-lines, as garland-like layers, disseminated in the perlite, or be in clusters. The gradual transition from single spherulites, embedded in the perlite, through spherulitic perlite to typical spherulitic rhyolite can be observed. Szterényi (11) mentioned regarding a similar rhyolite, that when the spherulites during their growth completely exhausted the uncrystallized space between each other, a different textural rock-type evolved. This "polyedrical spherulitic" type has no glassy groundmass, only spherulites, and generally breaks easily into small, angular pieces. The spherulitic rhyolite varieties occur on the southern and southwestern slopes of the hill, overlying the perlite-pumice-"level." Their greatest thickness, 18–20 m, is in the upper prospecting shaft.

Lithophysae Rhyolite.—The lithophysae rhyolite is a felsitic type containing many cavities ranging up to 1 cm in diameter. Mauritz (6) described the fillings and incrustations of the cavities as tridimite, hypersthene and "silica." The X-ray investigations established that the "silica" is amorphous glass. The few undulating bands of this type show the flow direction of the lava (Fig. 3). The lithophysae rhyolite alternates with vitric rhyolite types on the southern slopes namely with spherulitic types and with perlite. The maximum thickness of the lithophysae rhyolite is 25 m in the middle part of the hill. Here it occurs only above the spherulitic types.

Felsitic Rhyolite.—This is a dense, pink, lilac, lilac gray rock. The groundmass is completely crystallized. The X-ray analyses show the composition of this rhyolite type as 50 percent plagioclase feldspar and cristobalite, and 50 percent quartz. The felsitic rhyolite has a massive appearance in the quarries and exhibits nearly vertical joints. Banding is not common.

This rhyolite type occurs directly overlying the lithophysae rhyolite and has a maximum thickness of about 60 m. Both the lithophysae and felsitic rhyolites have been quarried.

CHEMICAL COMPOSITION AND GENETIC PROBLEMS OF THE COMPLEX

According to several sources (1, 2, 14), differences in the chemical composition, notably in the quantities of alkalis and alkali metals, may play a part in the formation of the vitric rhyolite varieties. The large number of samples investigated fairly represent the whole complex. The range of variation in the quantities of the elements present is demonstrable with a near-statistical accuracy. The problem of a false genetic evaluation, based on the results of a few analyses, could thus be avoided; the greater number of chemical analyses offer a more exact picture of the chemistry of the original lava flow.

Apart from the water content, the chemical compositions of the tightly interwoven, alternating vitric rhyolite types show no real differences. They reveal the same average values and the same range of variations of the minimum-maximum values. This proves the petrochemical homogenity of the entire complex. The magnitude of the range of variation of the individual components is proportional to their percentages (Table 1). The accessory and trace elements also have a rather uniform quantitative distribution. They are also present in the underlying andesite rocks. The results of the geological, as well as of the chemical investigations suggest that the rhyolite types owe their formation to differences in temperature and in the rate of cooling; both are intimately connected with each other. The water may be derived partially from transvaporization, described by Szádeczky-Kardoss (9), from the water-rich loamy, tufaceous wall of the volcanic pipe, and from rocks on the surface, also possibly from shallow ponds. The lava may have also brought up water of deeper origin (magmatic water, Varju). The author has found isolated, long, gray inclusions of rock even within the *uppermost* levels of the felsitic rhyolite type. Due to included, optically amorphous laminae of perlitic rhyolite they contain 1.8 percent of $+ H_2O$. This locally accumulating water must have been derived from a deeper, at least subsurface location.

The extreme variability of the rhyolite types is well illustrated in the southern part of the hill. The vitric types (pumaceous, perlitic and spherulitic rhyolite varieties) alternate not only among themselves, but also with non-vitric types. On the lower levels of the southwestern side of Kishegy, fine-grained lithophysae rhyolite alternates with perlitic-spherulitic rhyolite and overlies a band of interwoven lithophysae and spherulitic rhyolite. Felsitic rhyolite occurs near this locality; such a low-level occurrence is unusual on the hill. Here the felsitic type alternates with polyedrical spherulitic rhyolite. One of the most conspicuous alternations is between the light-gray spherulitic rhyolite varieties and the medium-deep-gray perlite (Figs. 2, 3). This phenomenon is exposed in the upper prospecting shaft of the southwestern slope and surrounding area, as well as in the bed of the creek, south of

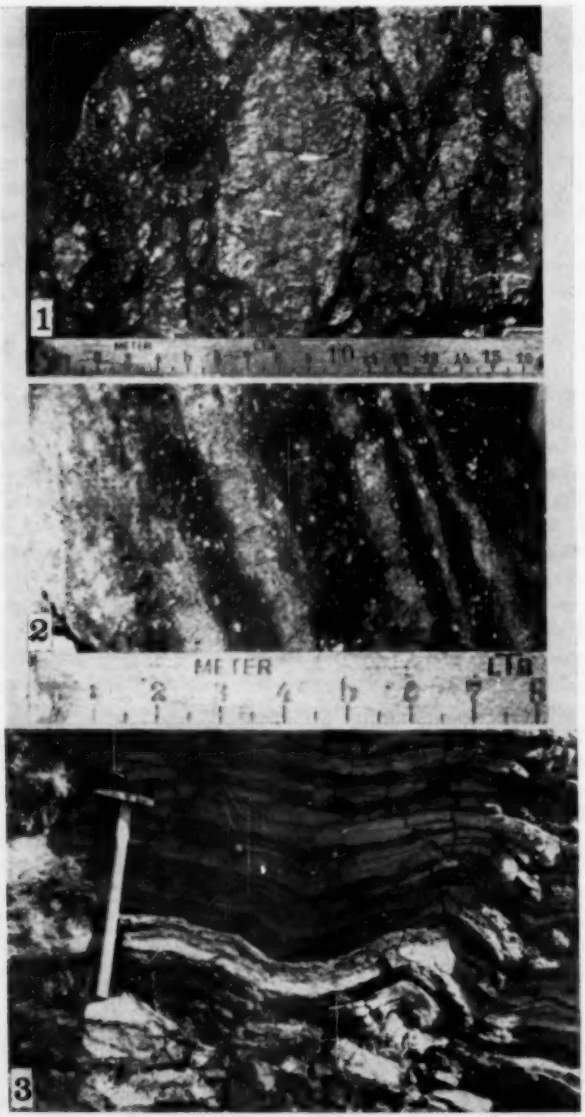

FIG. 1. Speckled alternation of perlitic (dark) and spherulitic-polyedrical spherulitic (light) rhyolite. Upper prospecting shaft.

FIG. 2. Alternating laminae of perlitic and spherulitic rhyolite. Upper prospecting shaft.

FIG. 3. Undulating bands of lithophysae rhyolite in the large southwestern quarry.

the hill. The different rhyolite types are present in irregularly-shaped nests, reaching several centimeters in thickness, and as parallel- and "cross-stratified" laminae of the same dimensions. According to two pairs of chemical analyses, the only difference between the two types lies in their water content. The perlitic laminae contain 0.8–1.0 percent more $+ H_2O$, showing the separation of "wet" and "dry" phases in the flowing and cooling original lava.

The TG-analyses established that the water-rich rhyolite types lose with varying speed most of their water content between 300–550° C (Fig. 5). The speed of heating was 10–12° C per minute. The sensitive DTA and DTG instruments indicated the water-loss with small-amplitude thermal peaks (Table 2). When a slower, 3° C per min, heating-rate was employed, the water was lost between 150–400° C. The ascending and descending sections

TABLE 1

EXTREME PERCENTAGES OF MAIN, ACCESSORY, AND TRACE ELEMENTS OF ANALYZED SAMPLES FROM THE KISHEGY-RHYOLITE COMPLEX. (THE RANGES OF VALUES OF THE DIFFERENT RHYOLITE TYPES ARE PRACTICALLY THE SAME. ONLY THE SiO_2 AND Al_2O_3—VALUES WERE RECOMPUTED TO A THEORETICAL WATER-LESS COMPOSITION; FOR THE OTHER COMPONENTS THE DIFFERENCE IS INSIGNIFICANT.)

SiO_2	74.09–78.08	
Al_2O_3	12.13–15.11	
FeO	0.53–1.00	(vitric types)
	0.14–0.35	(lithophysae-felsitic types)
Fe_2O_3	0.56–1.21	(vitric types)
	1.12–1.75	(lithophysae-felsitic types)
Fe_2O_3 total	1.27–2.05	
CaO	1.18–1.95	
MgO	0.02–0.78	
Na_2O	2.08–3.76	
K_2O	3.40–5.09	
Mn	0.005–0.1	
Sr	0.001–0.1	Magnitudes for the accessory and
Ti	0.0005–0.01	trace elements are given by
Pb	0.001–0.01	Dr. I. Kubovics photometrically.
Ga	0.001–0.01	
Cu	0.0001–0.005	
Co	0.0005–0.001	
Sn	0.0005–0.001	

of the curve are much steeper and the peak higher, than before. Five samples from a perlite quarry of Pálháza, northeastern Hungary, offer interesting comparisons. (Hegyalja Mineral Mines and Mills Co. Laboratory, Mád.) The perlite samples contained 2.9 to 3.4 percent $+ H_2O$. Each of the samples was exposed to two-hour heating at 300°, 400°, 500°, and 600° C. The 300° C-heating caused a 70 to 82 percent water-loss and only after heating at 600° C did nearly all of the water content disappear. It seems, that although the water is not bound with microcrystalline energies in the glassy groundmass of the water-rich rhyolite types, a substantial quantity of it is strongly held mechanically. The water-loss is controlled only by the intensity and duration of the communicated heat. Compared with the pumice and perlite, the felsitic and spherulitic types show a different kind of water-loss, with non-characteristic small peaks (Fig. 5, III–IV).

In summation the principle rhyolite types of the Kishegy complex may have been formed in the following manner: After the lava poured over the surface, its lower portion contained relatively more, unevenly distributed water, than the upper parts, which had a lower, more homogenous water content. [The uneven distribution of water under different geological circumstances in a Queensland rhyolite complex in Australia is also mentioned by Bryan (1), who also quotes Shepherd. Several authors have emphasized the textural manifoldness of certain rhyolite occurrences and de-emphasized their chemical diversity (3, 5).] The irregularly dispersed water in the complex reflects the inhomogeneous physical conditions of the rhyolite-lava.

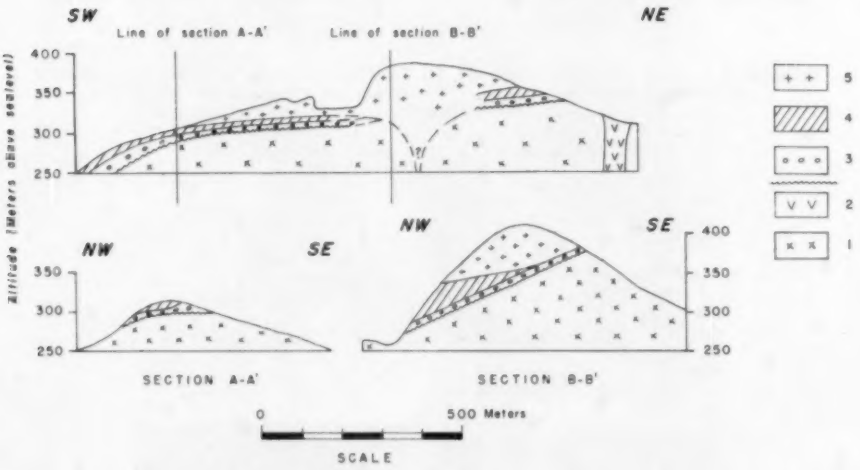

FIG. 4. Longitudinal (above) and transverse cross-sections (below) of Kishegy. 1. Andesite complex; pyroxene andesite and tuff (Miocene, Helvetian-Tortonian). 2. Pyroxene andesite dike (Miocene, Helvetian-Tortonian). 3. Vitric (pumaceous, perlitic, and spherulitic) rhyolite types. 4. Lithophysae rhyolite. 5. Felsitic rhyolite (3.–5.: Middle or Upper Miocene). Vertical exaggeration $\times 2$.

According to Szádeczky-Kardoss (9) pumice forms in the most-transvaporized parts of acidic lavas. In this complex the water-vapor was most abundant in certain parts of the lower levels of the lava flow. In other water-rich, fast-cooling parts unaffected by the volatiles during the solidification perlite was formed. In places, particularly above the perlite-pumice "level" where cooling was somewhat slower, the spherulitic types developed. Lengyel's work (4) on the formation of spherulites should be mentioned. He produced artificial spherocrystals from aqueous and aqueous-hydrochloric-acidic solutions of certain compounds, heating the solutions at a given rate and a temperature of 80° to 100° C.

In the rhyolite lava the presence of the water as a solvent does not seem to be a prerequisite for the formation of the spherulites. This is affirmed by the presence of embedded spherulites in the obsidian of Yellowstone Park (3). The spherulites there have a water content of 0.66 percent, compared with that of the obsidian, 0.62 percent. The fundamental cause for the spherulite formation in the rhyolite may be special temperature and cooling conditions, and centers as "seeds" for the crystallization.

The spherulitic rhyolite of Kishegy has been formed from warmer hydrous portions of the lava, where the consolidation was somewhat slower and

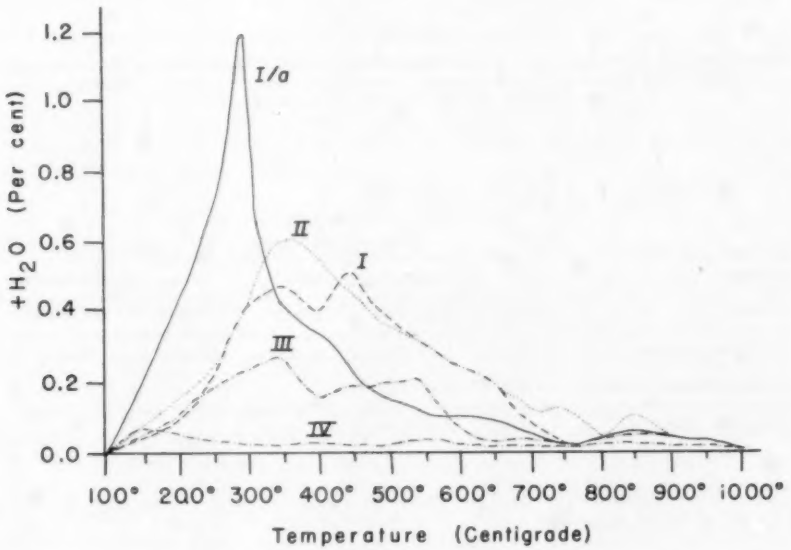

FIG. 5. Curves of water loss of the Kishegy rhyolite varieties. The data are plotted at 50° C intervals, heating speed: 10° C/minute. I. Pumice, lower prospect shaft. I/a. The same, heating speed 3° C per minute. II. Perlite from the southern slope of the hill. III. Spherulitic rhyolite, southwestern quarry. IV. Felsitic rhyolite, upper prospect shaft.

perhaps the water content lower, than that of the pumice and perlite. In the lava-masses, possessing a maximum aptitude for strained crystallization, the polyedrical spherulitic rhyolite type developed and the strongest dehydration took place. The lithophysae variety originated from gas-rich lava-sheets. It is possible that the lithophysae rhyolite, alternating with the vitric ones, received the water-vapor before solidification from the neighboring spherulite-forming lava sheets on the southern slopes of Kishegy. The water, squeezed out from these sheets, could enter the surrounding, warmer lava, and revaporize, thereby increasing its volatile content. The felsitic type is the

uppermost member of the series and represents the slowest and most "regular" solidification from a relatively water-deficient lava.

The four main vitric rhyolite types show indistinct water content boundaries (Table 2). The highest average H_2O-content of the pumice is due to strong transvaporization. Perlitic laminae, observed between over- and underlying laminae of pumice contain 0.5–0.8 percent less water than the pumice laminae, but otherwise have the same chemical composition. The lower water content of the spherulitic types indicates dehydration. It is interesting to note that the ferri : ferro-oxide ratios of the vitric varieties do not differ from each other in extreme values, nor in average-values (1.0–1.2). This relationship has no value in characterizing differences in the conditions of formation.

TABLE 2

OXIDATION AND DIFFERENTIAL-THERMAL PROPERTIES OF THE KISHEGY RHYOLITE VARIETIES. (THE DTA-PEAKS ARE ENDOTHERMAL; "NO AN.": NO ANALYSIS MADE. THERMAL PEAKS INDICATE THE WATER-LOSS FROM THE ROCKGLASS.)

Rhyolite type	$\frac{Fe_2O_3\%}{FeO\%}$	$+H_2O\%$	10° C/min	12° C/min	10° C/min
			Heating		
			DTA-peaks	DTG-peaks	DTG-peaks
Pumice	0.7–1.7	3.48–4.57	400° C	no an.	380–390° C
Perlite	0.6–2.0	2.41–3.70	380° C	300° C	370–380° C
Spherulitic rhyolite	0.8–1.4	1.20–2.66	no an.	300–330° C	400° C
Polyed. spher. rhyolite	0.9–1.9	0.41–1.02	—	—	—
Lithophys.-felsitic rh.	3.3–9.6	0.65–1.39	—	—	—

COLOR OF THE RHYOLITE VARIETIES

Those varieties that resulted from faster cooling from a lava with an originally high water-content are dominantly gray. No connection could be found between the deepening of the color and the water-content and oxidation relations of the perlites. The felsitic and lithophysic types exhibit a higher oxidation value and have mainly a reddish, pink, lilac color as the consequence of their slower solidification. The coloring mineral could not be established with microscopic and X-ray-diffraction methods because of its small size and maximum 1.5 percent quantity. The deeper red samples contain more Fe_2O_3 than the pink ones, thus suggesting the type of coloring compound that may be present. The lilac coloring of rocks is generally explained by the presence of manganese or vanadium. The MnO content of several felsitic rhyolite samples is only 0.06–0.09 percent. In one of the medium-lilac samples the manganese was present only as a "trace." Similarly no regular

TABLE 3

COLOR AND IRON OXIDE CONTENT OF FELSITIC AND LITHOPHYSAE RHYOLITE SAMPLES FROM KISHEGY

Color	Fe_2O_3%	FeO%	Color	Fe_2O_3%	FeO%
Pale lilac	1.12	0.15	Pale red, pink	1.27	0.23
	1.28	0.16		1.29	0.27
Medium lilac	1.75	0.20	Lilac red	1.55	0.24
	1.76	0.14			
	1.78	0.23	Bright red	2.12	0.22

differences could be recognized in the Mn content of red, pink, and lilac samples. The lilac and reddish-pink samples show the same Fe_2O_3 and FeO values (Table 3) and ratios. The iron content increases with the deepening of the red and lilac color. After heating or moistening the original color of some felsitic rhyolite samples changed markedly. Therefore this factor is also involved in the problem.

POSTVOLCANIC EFFECTS

The postvolcanic activity in the Kishegy complex is represented by the alteration effects of solutions rising through magmatectonic and tectonic fissures. The solutions leached the coloring agents of the rock and precipitated the partly limonitized iron content in concentric bands in the upper zones. There are hydrothermal brown clay fissure-fillings containing 80 to 90 percent Ca-montmorillonite and cristobalite and quartz, 5 percent each. There are also light-gray pelitic fillings, some containing only plagioclase feldspar, and others with up to 30 percent sanidine feldspar. In addition to the accessory and trace elements in the rhyolite, these fillings also contain: Ni, Cr, Ge, V, and Zn. Compared with the feldspathic filling, in the brown clay there is, in order of magnitude, more: Mn, Ti, V, Cu, Cr, Ga, Zn, Ni and less Sr, Sn and Ge. Other products of similar alkaline postvolcanic solutions are yellowish brown wax-opal cavity fillings, reaching 40 cm in diameter, and red and white translucent opals. Water-clear, amorphous opal-like fillings also occur. In the pumice on the southwestern slope of Kishegy greenish yellow Ca-montmorillonite grains have developed. The postvolcanic effects caused no substantial alteration of the complex as a whole.

The lithophysae and felsitic rhyolite has been quarried since about the XIVth century mainly as building material. In the past it was also used for making millstones. The felsitic rhyolite especially has all the properties of a first-class building stone, including cleavability and resistance to weathering. The perlite and pumice have been recently investigated for potential use in the modern building industry.

CONCLUSIONS

The formation of the various rhyolite types of Kishegy is due not to chemical differences in the composition, but to physical causes. In the glassy

groundmass of the water-rich vitric varieties the water is mechanically bound. The conditions of formation depended on the absorption and loss of water, and on the temperature, both intimately connected with each other. A great variation in the water content of the lower part of the rhyolite complex is due to heterogenous physical conditions prior to the consolidation. The reddish and lilac rhyolite types are colored by a Fe_2O_3-mineral, probably hematite, which may be present in minute quantities.

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METALLOGENIC MAPS[1]

A. H. LANG

ABSTRACT

Published metallogenic maps and literature concerning them show much variation in objectives, terminology, and methods of representation. This review of early and recent examples is offered because it is evident that distributional studies and maps to illustrate them are increasing, and that more agreement on terminology and other matters is desirable. The main conclusions are that the term "minerogenetic" is preferable if non-metals as well as metals are treated; that metallogenic or minerogenetic maps should illustrate provinces, not mineral economics, unless the latter is done incidentally and without detracting from metallogenic detail; that standard metallogenic maps should deal with recognizable mineral occurrences or places where more than "trace" amounts have been shown by assays; and that maps showing distribution of smaller amounts of metals should be regarded as special metallogenic maps treating trace-element or geochemical data.

INTRODUCTION

INTEREST in metallogenic provinces and metallogenic maps has increased greatly during the last few years. Publications show considerable variations in terminology and objectives. Correspondents have expressed doubt as to what a metallogenic map is or should be, and a committee has requested organizations in various countries to experiment. The following brief review may be of use to others in forming their own opinions, even if they do not agree with the writer's conclusions. There are many indications that research and publications on the subject are about to expand, so closer agreement on terms and principles would be in order. Early definitions and usages are summarized and all published maps called metallogenic (or analogous names) known to the writer are described briefly, together with a few that bear some relationship but have not been so called. Except concerning definitions and other matters affecting maps, the paper does not attempt to deal with the subject of metallogenic provinces, which has been reviewed recently by Bilibin (3), Turneaure (36), Shatalov (30) and others.

The writer is greatly indebted to Dr. P. W. Guild for reading the manuscript and offering helpful suggestions.

BACKGROUND TERMINOLOGY

The first uses of the terms 'metallogeny' or 'metallogenesis' appear to be those of de Launay (11, p. 6; 12, p. 559) who stated that the purpose of metallogeny is "to study abnormal concentrations of metals in their natural deposits." Holmes (18, p. 155) defines metallogeny as "the genetic study

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of ore-deposits in relation to age, regional tectonics, and petrographic provinces."

The concept of metallogenic provinces was developed by de Launay from 1897 and Spurr from 1902 in a series of publications (see references). De Launay used the expression "zones métallifères" in his earlier papers and "provinces métallogéniques" in 1910 and 1913. The 1910 paper deals with minor constituents of sphalerite, such as cadmium, bismuth, and germanium. In his Traité de Métallogénie (13) he used the term "provinces" mainly to distinguish regions metallized in a general way from unmetallized ones, but included some distinctions based on kinds of deposits.

Spurr took up the subject in the following passage (31, p. 336):

> Our inquiries lead us to the hypothesis that by magmatic segregation the metals of commercial value, as well as the other rock-forming elements, are irregularly and to a certain extent independently concentrated in certain portions of the earth's crust. Such portions, characterized by the relative abundance of certain metals, may be called metalliferous provinces. It is in these provinces that orebodies will generally occur. The provinces may or may not be closely identified with petrographic provinces (divisions based on the relative abundance of the commoner metals and other elements), although, by reason of the chemical affinity which exists between certain of the commoner elements, they probably generally do so, to a certain extent at least.

He referred to this quotation in 1905, adding that perhaps a better name would be metallographic provinces, and he used that term in a paper in 1907 and in a book in 1923. Ransome (26) criticized Spurr's term "metallographic" and advocated "metallogenetic."

Maclaren applied the province concept in his monograph on gold, stating (23, p. 43):

> The most natural grouping of the world's gold-deposits appears to be reached by a combination of geographical and geological data, resulting in the establishment of fairly definite auriferous provinces, well separated from each other either in time or in space, or in both. The individual members of each group possess strong affinities that can hardly be coincidental. The classification here adopted is to be regarded as merely preliminary, for it must certainly be modified with progress in the knowledge of ore-deposits. Its general value is considered to lie largely in the fact that the differences between auriferous provinces, no less than their resemblances, are emphasized.

Lindgren (21) coined the word "minerogenetic," evidently to provide for consideration of non-metalliferous occurrences as well as metalliferous ones, in the statement: "Over larger or smaller areas the conditions may at a given time be favorable for the deposition of useful minerals. Such areas are called minerogenetic or metallogenetic provinces." The name "minerogenetic" was used in later editions of his book, and Bateman (1) mentioned it in 1942. When reviewing the second edition of Bateman's book Cameron (9) commended the extension of the subject to non-metals and advocated abandonment of "metallogenetic" in favor of "mineralogenetic" or "minerogenetic."

In a paper (7) published in 1933 Buddington reviewed the relations between kinds of igneous rocks and kinds of mineralization, and between the

degree of differentiation in magmas and related mineral deposits. He considered that a metallogenetic or metallographic province may, but need not necessarily coincide, with a petrographic province, and concluded (p. 355):

> In addition to a variation in the metal content of the potential magma zone from one province to another, there may also be a variation in the amounts of each of the volatiles present. . . . This may have a very important influence in determining the course of magmatic differentiation and in particular the kind and quantity of metals which are extracted from the sub-magmas to form ore deposits.

Turneaure reviewed the subjects of provinces and epochs in 1955 (36). For the purpose of his review he defined a province as follows (p. 40):

> the term metallogenetic province is used in a broad sense to refer to strongly mineralized areas or regions containing ore deposits of a specific type or groups of deposits that possess features suggesting a genetic relationship. To apply consistently a more precise definition would require a greater uniformity of opinion than now exists as to processes involved in the formation of the ores and the epochs during which ore deposition took place. Nevertheless, the connection between ore deposition and orogeny permits a grouping of the metallogenetic provinces according to their tectonic setting: the Precambrian shields, the stable regions, and the mountain belts.

Russian geologists have been interested in metallogenic provinces for many years. According to Betekhtin (2) early generalizations on the localization of mineralization and on forecasting the distribution of new discoveries were made by Obruchev, Fersman, and several others.

> In the latter half of 1930's S. S. Smirnov directed this research towards a new course and thereby has laid the foundation of the regional metallogeny as a branch of science on ore deposits. S. S. Smirnov and his disciples developed the conception of the zonal arrangement of tin, tungsten, molybdenum, gold and other metals over the vast territory of Eastern Siberia and the Far East. The established metallogenic provinces against the background of the geological structure and geological history of the development of the earth's crust, enabled us to bind into a single unit the isolated ore regions and individual occurrences and predict the presence of new ore-bearing regions in the vast spaces between these regions and occurrences. . . . A great merit in the further development of the problems of regional metallogeny belongs to Y. A. Bilibin, who has organized within the All-Union Geological Scientific Research Institute of the Ministry of Geology a collective of members entrusted with the study of the regularities of the distribution of ore occurrences in different ore-bearing regions of our country.

EXAMPLES OF METALLOGENIC AND OTHER MAPS

The first map called metallogenic appears to be one inserted in de Launay's paper on "La Métallogénie de l'Italie" (12). This is a colored map on the scale of 1:2,000,000, called "Carte Métallogénique de l'Italie septentrionale et centrale." The colors indicate geological map units. Symbols such as 'Or' and 'Cu' indicate scattered occurrences of gold, copper, nickel, iron, chromium, lead, zinc, mercury, and complex sulfides. Petroleum is also shown. A smaller map of approximately the same area is inset in one corner and called "Carte métallogénique de la region italienne." This map carries colored units depicting: "Zone du mercure"; "Zone des filons

sulfurés plombo-zincifères"; "Zone de petrole"; "Zone des roches vertes avec faciès métamorphiques, imprégnations sulphureuses et gites de ségrégation"; and "Massifs anciens, à minerais filoniens probablement d'âge hercynien." Essentially the same map is reproduced in black-and-white in "Traité de Métallogénie" (13, p. 257) and is the only other illustration called a metallogenic map found in de Launay's publications. Spurr's writings contain figures illustrating belts, but none called a metallogenic or metallographic map or diagram.

Maclaren's book (23, p. 46) contains a page-size "Sketch Map of the World, Showing Distribution of the Principal Auriferous Provinces." Four patterns indicate areas of: (1) Archaean schists; (2) Precambrian basic intrusions; (3) Granodiorite; and (4) Tertiary andesitic goldfields.

A paper by Finlayson (16) on "The Metallogeny of the British Isles" contains a small inset map on the scale of 1 inch to 60 miles. This is titled "Metallogenetic Map of the British Isles," but it merely shows the areas influenced by the Caledonian, Hercynian, and Armorican orogenies without positions of deposits. A table in the paper relates these areas to metallogenic epochs and to classes of deposits typical of them, but does not name any specific deposits. It seems, therefore, that the map would more appropriately have been called orogenic instead of metallogenic.

In 1957 the Geological Survey of Japan began publication of a series of four interesting maps called "Mineral Provinces of Japan," showing mineral deposits formed in Quaternary, Neogene, Mesozoic to Paleogene, and Palaeozoic times. Rocks of various kinds and ages are indicated by colors, and symbols illustrate patterns of mineral deposits, which are classified to some extent both genetically and mineralogically. The devising and reproduction of the symbols is excellent, but the user of the maps is left to decide for himself regarding the extent of the provinces.

Search of a number of publications, indexes, and bibliographies failed to reveal other maps called "metallogenic" or analogous names issued before 1958, although there may be some that were not found. Maps and diagrams showing positions of mines, mineral occurrences, and "mineral belts" have, of course, appeared frequently. The following Canadian examples are cited because they are best known to the writer.

A map called "Mineral Map of Canada" (No. 232), published in 1914 by the Mines Branch, Department of Mines, contains on a non-geological base symbols for principal metal and non-metal deposits, including coal, oil shale, petroleum, and natural gas. This was the forerunner of a series of maps called "Canada, Principal Mineral Areas" (No. 900 A), now in the tenth edition, prepared jointly by the Mineral Resources Division of the Department, and the Geological Survey of Canada. Known popularly as the "Mineral Map of Canada," this shows much the same kind of information as the one mentioned above, but on a much simplified geological base; production charts and small inset maps showing supplementary economic data are added. Also, the Geological Survey of Canada has published geological maps on the scale of 1 inch to 20 miles for most of the political provinces and territories of the country. Mines and a few prospects are indicated on

some of these, and others are accompanied by separate non-geological maps called "Mineral Maps," but even these show only producing mines and some of the better-known prospects. The Geographical Branch of the Department published in 1957 an Atlas of Canada including maps dealing with non-ferrous metals; primary iron and steel; industrial minerals; and mineral fuels, pipelines and refineries. These show principal deposits only, on non-geological bases; size of production is indicated by circles of different diameters drawn around the symbols; total production of the country is shown by inset charts. We have not regarded as metallogenic any map discussed in this paragraph.

In 1953 the Ontario Department of Mines published a "Mineral Map of the Province of Ontario" (No. 1953A; Revised ed. 1957A). This is much the same type as "Canada, Principal Mineral Areas," the main difference being that the larger scale (1 inch to 20 miles) permits showing a few prospects as well as producing mines. A colleague in another country mentioned in a letter that he considered this the best metallogenic map he had seen. It is an excellent map, but it is doubtful whether the compilers regard it primarily as metallogenic. True, it relates principal deposits to regional geology, but only a fraction of the known mineral occurrences are indicated, and those are not subdivided into geological or genetic classes. The writer believes that it can be regarded as a "threshold" example of a metallogenic map, and that the same can be said of "Canada, Principal Mineral Areas."

An interesting map relating principal mining camps and tectonic features in southern British Columbia and northwestern United States was prepared by Billingsley and Hume (5, p. 546) and called "Tectonic map of northwest Boundary region." It followed other studies by Billingsley and Locke (6) and Billingsley (4).

A map accompanying "Les Gites Plombo-Zincifères de Tunisie" by Sainfield (27) shows principal geological features (including tectonic) in black-and-white patterns and one color. Deposits are indicated by four symbols, for veins, replacements, impregnations, and mixed deposits. Although not called so, this can probably be regarded as one type of metallogenic map.

In a paper on "Metallogeny of Ore Districts" Shatalov (30, p. 28) discusses possibilities for construction of metallogenic maps, advocating three basic types of maps: (1) regional predictions based on provinces or zones illustrated on maps not greater than 1:500,000; (2) medium-scale investigations of ore districts, usually at scales of 1:50,000 or 1:25,000; and (3) large scale predictions at 1:10,000 or greater.

In 1956 a sub-committee to plan a metallogenic map of the world was established by the International Geological Congress. As a first step, each country was requested to prepare an experimental "mineral map" that could be compared with its geological and tectonic maps. Specifications included showing mineral deposits, excluding building materials, in as much detail as practicable, and indicating sizes of deposits and as much other pertinent data as could readily be tabulated; it was also suggested that genetic classifications be avoided. Each country was also asked to prepare separate maps for iron and coal, as experiments in dealing with one product only.

The Geological Survey of Canada had already published two maps illustrating Canadian coalfields, including economic data (22), and proceeded to experiment with other maps, most of which are on transparent paper and on the scale of 1 inch to 120 miles, to permit comparison with the Geological Map of Canada. One showing medium and large producing and formerly-producing mines, including non-metalliferous ones as requested, was submitted to the committee in manuscript form. Metals were differentiated by colors and, to follow the recommendation to avoid genetic classifications, a separation into veins, disseminations, massive deposits, and placers was indicated symbolically. The term "placers" is genetic but the origin is so obvious that it seemed suitable. Several maps for individual metals were prepared, four being published to date. These deal with beryllium (37), uranium (19), iron (17), and molybdenum (38). The map for iron shows bands of iron formation and other concentrations, but, of course, omits the ubiquitous minor occurrences. The other maps, however, show all known recognizable mineral occurrences or areas containing many occurrences, or places where the metal has been shown by assays to occur in more than "trace" amounts. Symbols indicate semi-genetic classifications. On the map for uranium an attempt was made to forecast regions favorable for further discoveries. The published and unpublished maps, together with other data, were collated to form two preliminary "composite" maps, one for major metals and one for minor metals (20).

The United States Geological Survey, in co-operation with the United States Atomic Energy Commission, published in 1959 three maps illustrating "Epigenetic Uranium Deposits in the United States" (15). Use of colors outlines broad groupings of sedimentary, igneous, and metamorphic rocks, and symbols indicate veins, concordant deposits, and ages and kinds of host rocks. The information is based on occurrences or groups of occurrences where recognizable uranium minerals or assays of 0.01 per cent U_3O_8 or more were obtained. These maps are not called metallogenic but they seem to be useful examples of such maps and to indicate one way in which data of this kind can be presented effectively.

A study of "Metallogenic Provinces of the Southwestern United States and Northern Mexico" by Burnham (8) is accompanied by eight maps for which patterns and sizes of symbols were employed. Burnham pointed out that de Launay and Urbain recognized the existence of trace-elements in sulfide minerals but that little emphasis was placed on the geographical or province aspect of such relationships until 1940 when Stoiber (35) showed that similarities in compositions of sphalerite existed within metallogenetic groups. This concept was augmented by studies by Warren and Thompson (39) and Schroll (28, 29). Burnham applied this method to study of the distribution of trace-elements in chalcopyrite and sphalerite, illustrated by five uncolored maps in which patterns are skilfully employed. Three others, dealing with silver, gold, and copper deposits, illustrate positions, production, and reserves, but not trace elements. The paper by Warren and Thompson contains a small sketch-map and the other papers are unillustrated.

The Soviet delegation provided in 1958 printed legends for a Map of

the Mineral Resources of the World and a Metallogenic Map of the U.S.S.R. (scale 1:5,000,000). These detailed legends, using colors and symbols, indicate important undertakings.

A Metallogenic Map of the World compiled by Magakyan was described by him (24) as on the scale of 1:22,000,000, relating geological structural elements with principal mineralization processes and recognizable variations in the distribution of metallic ores. Basement and platform shield areas and five ages of mobile folded belts are differentiated. Deposits are classified genetically and divided into very large and other "industrial" ores. Magakyan discusses the division of factors controlling metallogeny into primary and secondary factors, depending on whether they can be shown on small-scale or large-scale maps. His paper is illustrated by a black-and-white figure on the scale of 1:100,000,000, described as a schematic representation of the map itself. The figure is interesting and informative, but the scale permits showing only the broadest "provinces" and a few selected mines or mining camps; no doubt the larger map is more detailed.

Petrascheck (25), commenting on the proposal for a map sponsored by the International Geological Congress, criticized, as others have done privately, use of the name metallogenic where non-metals are included, and suggested that, if genetic classifications are not to be used, the term "geological mineral-deposit map" would be more suitable. He advocated that the map should show the typical characteristics of each mineral deposits province, that symbols should indicate the shapes and contents of the deposits, and that size should be based on both production and reserves.

CONCLUSIONS

The terms "metallogenic" and "metallogenetic" are well established and there is little choice between them; the former may be preferable because it is a little shorter. The concept of provinces embraces areas of all sizes but the word "province" normally implies a fairly large area, therefore in many contexts it seems best to speak of metallogenic sub-provinces, areas, belts, or lineaments. The term "region" may be preferable for the largest areas.

It does not seem practicable or necessary to adhere to a rigid, detailed definition of what constitutes a metallogenic map, but certain limitations are advocated. First, use of the term "metallogenic" for maps that deal more than incidentally with non-metals is confusing and illogical. There seems no great objection to adding, as de Launay did, one or two non-metals or fuels to a map called metallogenic which otherwise deals with metals, but for maps that treat non-metals or fuels more extensively than that, why not use Lindgren's term "minerogenetic," or "mineralogenic"? Secondly, the writer considers a metallogenic or mineralogenic map to be essentially one that illustrates the spatial aspects of metallogenesis or minerogenesis, in other words, one that illustrates metallogenic or minerogenetic regions, provinces, or smaller areas. To do so it is desirable to use as much empirical or statistical data as possible, by plotting most or all known occurrences, not merely

to plot relatively few, selected occurrences. A map of this kind may treat only a single metal, or a few related ones, or be a "composite" map dealing with several metals. If occurrences or areas of occurrences can be differentiated according to various classes of deposits, so much the better, but to do so for a map called metallogenic or minerogenetic a genetic or semi-genetic classification seems to be required. There are objections to genetic classifications, mainly because the origins of some deposits are in doubt, but it seems feasible and desirable to use for such a map a classification that is at least semi-genetic, i.e. one which avoids the more controversial terms such as "hydrothermal." Some indication of the relative importance of deposits may well be added if this does not make the map too complicated, because it is useful to distinguish between areas known to contain deposits of commercial value and areas that contain only mineral occurrences or unproved deposits, but the essential objective should not be disregarded or weakened; a map can readily be made so complicated that its effectiveness is destroyed. If, on the other hand, the main purpose is to show the positions of mines, and perhaps to add data for production, the terms "mining map," "mineral deposits map," or "mineral economics map" seem much more appropriate. The writer favors "mineral economics" if figures for production or "proved" reserves are added. He questions the suitability of using "mineral resources" instead, because so much of total mineral resources are in the form of partly-proved or completely unrevealed reserves, and based mainly on geological forecasts, that a resources map is regarded as still another type. Incidentally, it may be remarked that publication of data on reserves is rendered difficult because some organizations do not permit release of such information, and because methods of estimation are not standardized. The term "mineral map" seems best for maps whose main purpose is to show the positions of mineral occurrences as such, without stressing their economic importance, or their illustration of metallogeny; this name seems suitable whether or not the map also contains background information on areal geology.

It is highly desirable that metallogenic data be relatable to regional geological patterns, including tectonics. This is difficult to achieve on a single map if the data are complex. Therefore it seems acceptable to term a map metallogenic if no geological data are included, and even if the map is on ordinary paper, because it can be placed beside a geological map. The use of transparent overlays proved to have many advantages, but also the drawbacks of being not well suited for folding and of being more costly. The method used by de Launay, of showing geology and positions of mineral deposits on one map, and the metallogenic "zones" interpreted from them on another printed on the same sheet, is a way of handling the problem which distinguishes clearly between the empirical data and the inductions.

The writer believes that the more standard types of metallogenic maps will be those dealing with recognizable mineral occurrences or places where more than "trace" amounts of the metal concerned have been demonstrated by assays. Several experimental maps prepared during the last few years have been based on "cut-offs" of the order of 0.01 per cent. It seems undesirable to attempt complete uniformity in this regard, because some metals are so

much more abundant than others. Guild (personal communication) suggested that this could be overcome by adopting some factor of the clarke for each metal. Studies and maps treating still smaller amounts appear to offer great possibilities as well, but if they are primarily of this kind it would be preferable to call them "geochemical" or "trace-element" maps. If they include data for both the more normal occurrences and minute amounts, they might well be called metallogenic and the words "including geochemical data" or "including trace-element data" could be added. Other special kinds of metallogenic maps that seem to offer challenging opportunities would be those indicating mineralogical and wall-rock associations; relationships to kinds of igneous rocks; associations of two or more metals in amounts greater than "traces"; and quantitative maps, treating relative abundance by one of the methods used to illustrate population and other densities, and dealing either with numbers of occurrences only, or with numbers and sizes.

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SCIENTIFIC COMMUNICATIONS

THE USE OF CLINOPTILOLITE TO REMOVE POTASSIUM SELECTIVELY FROM AQUEOUS SOLUTIONS OF MIXED SALTS[1]

L. L. AMES, JR. AND B. W. MERCER

During previous studies of the cation exchange properties of clinoptilolite (1, 2) aimed at removal of cesium from mixed salt solutions, another potential use for clinoptilolite was indicated. Use would be based on the existence of an "intensified" cation replacement series characteristic of clinoptilolite (2), and the fact that natural potassium-containing mixed salt solutions, such as sea water, contain very little cesium or rubidium (3). Thus the potassium present in such natural mixed salt solutions could be concentrated, relative to the amount of potassium in the original solution, by passage through a sodium-based clinoptilolite column. Some data concerned with selective potassium removal from mixed salt solutions by clinoptilolite, and their possible application to a potash recovery process, are reported here.

The general replacement series for the alkali metal and alkaline earth metal cations were reported previously (1) as $Cs^{+} > Rb^{+} > K^{+} > Na^{+} > Li^{+}$ and $Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2}$. At $pH < 3$ the exchange of alkaline earth metal cations onto clinoptilolite is practically nil, while alkali metal cations are little affected by the increased H^{+} competition. Clinoptilolite offers a means of separation of the two cation series.

Loading and elution curves for the inert constituents were obtained during investigation of trace cesium removal and recovery from process solution containing a mixture of salts. The salt solution, the composition of which is given in Table 1, was passed through a column containing 50 g of 0.25 to 1.0 mm, sodium-based clinoptilotile.

Figures 1 and 2 are potassium breakthrough curves for clinoptilolite and the influent composition given in Table 1. Adsorption experiments at two different flow rates gave the results shown. The potassium capacities calculated from these breakthrough curves are 58.1 meq K^{+} per 100 g clinoptilolite at a flow rate of 236 ml/cm^2/hr and 63.4 meq K^{+} per 100 g clinoptilolite at 750 ml/cm^2/hr. Clinoptilolite potassium capacity is probably little affected by the indicated flow rate change, and therefore averages about 60 meq K^{+} per 100 g clinoptilolite.

The 50 g, potassium-loaded (and Cs^{137}-loaded) clinoptilolite column was

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TABLE 1

CHEMICAL COMPOSITION OF THE PROCESS SALT SOLUTION CONTAINING POTASSIUM

Salt	Salt weight, g/l	Salt molarity	Solution pH
NaCl	26.844	0.495	
$MgCl_2 \cdot 6H_2O$	10.635	5.32×10^{-2}	
$CaCl_2 \cdot 2H_2O$	1.467	9.97×10^{-3}	
KCl	0.725	9.72×10^{-3}	6.4
$SrCl_2 \cdot 6H_2O$	0.040	1.50×10^{-4}	
$Cs^{137}NO_3$	—	1.74×10^{-8}	

then eluted with a saturated solution of NH_4Cl. The potassium and sodium contained in the eluate after passage through the column is given in Table 2. A column volume, in all cases, refers to a 63 ml volume of effluent solution.

Recent work has shown that elution with a saturated NH_4NO_3 solution would remove the potassium in approximately half of the number of column

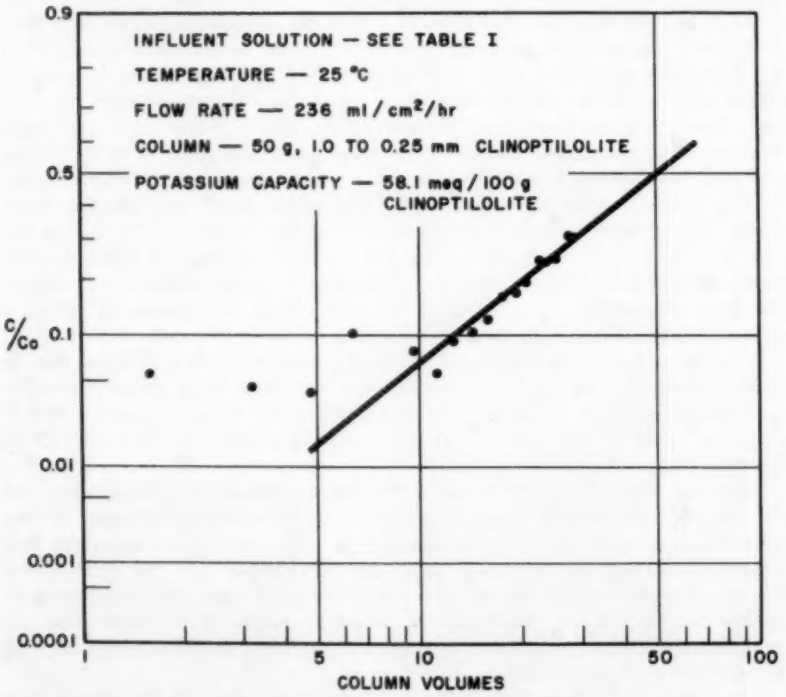

FIG. 1. Potassium breakthrough curve for clinoptilolite at a flow rate of 236 ml/cm²/hr. The constant potassium leakage shown in both Figures 1 and 2 suggest that both of the indicated flow rates are too rapid for optimum K^+ removal.

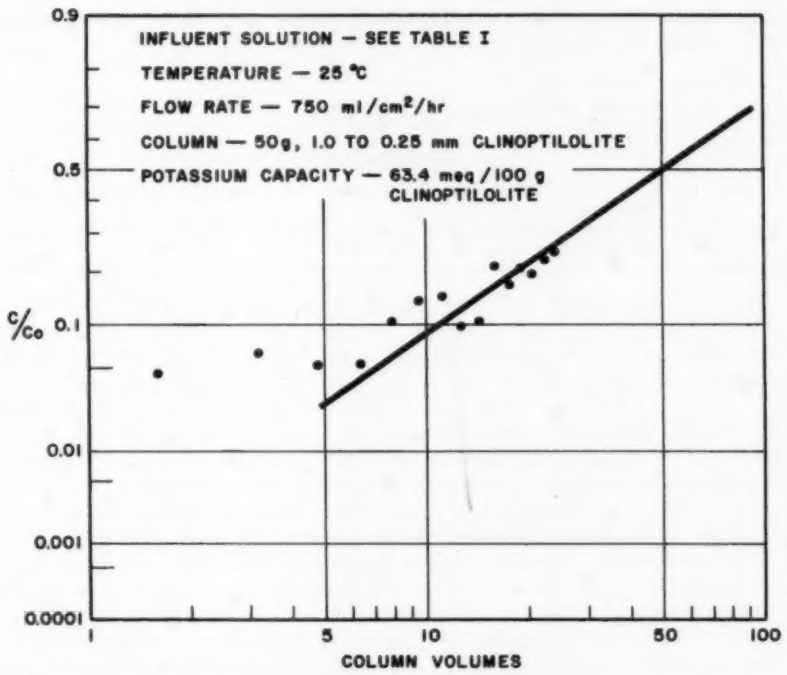

FIG. 2. Potassium breakthrough curve for clinoptilolite at a flow rate of 750 ml/cm²/hr.

volumes required using NH_4Cl. The acid resistance of clinoptilolite also makes acid elution feasible, but a greater quantity of acid than NH_4Cl is required for K^+ elution.

Much more work would be necessary to develop a recovery process, but the results presented here show that the potassium specificity of clinoptilolite

TABLE 2

SODIUM AND POTASSIUM CONTAINED IN THE ELUTING NH_4Cl SOLUTION FROM COLUMN OF FIGURE 2

Column volumes	K^+, mg/l	Na^+, mg/l
1.6	8660	8510
3.2	1950	560
4.8	940	100
6.4	720	7
8.0	103	4
9.6	23	2
11.2	7	2
12.8	4	2
14.4	2	2

Effluent solution pH = 6.3

may allow the extraction and recovery of potash from mixed salt solutions on a commercial scale.

General Electric Co.,
Richland, Washington,
July 1, 1961

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DISCUSSIONS

ORE DEPOSITS AND SEDIMENTARY FEATURES IN TENNESSEE

Sir: Dr. Ohle's comments (3) on my paper (1) on some features of the Jefferson City mine are well put and emphasize two main points: the importance of the vug-filling sand in ore deposit chronology, and, the deficiencies of a syngenetic hypothesis of origin. I would like to make these further comments.

At the time of writing, now more than two years ago, relatively few observations of the "sand" had been made and interpretations were tentative, recognizing the uncertainties arising from limits of error in measuring the concordance of sand and country rock dips, and the paucity of data. In the intervening time however, many hundreds of observations have been made, a large number of which have been preserved in detailed photographs. Although not every exposure of sand displays good laminations, in none of the localities exposed to date have the laminations shown clearly a discordant relationship with country rock bedding. One misconception which I should like to correct is that the filled vug had "no determinable inlet or outlet." Although the ground is now nearly solidly filled with dolomite of various origins, it is clear that during the time of sand deposition circulation was abundant and vigorous. The pebble-filled vugs (1, p. 994) while much rarer, always occur in areas of abundant sand. Recently a few rounded fragments of sphalerite imbedded in sand were removed and discovered to be pebbles cemented in place by the surrounding sand.

When the possible significance of the vug-filling sand was pointed out to district geologists, the existence of this sand in identical relationships was reported from all mines of the district. Mr. James E. Ricketts pointed out to the writer and several other geologists an occurrence at Mascot where the country rock dips about 15 degrees and the sand laminations were concordant. Similar material has been found in The New Jersey Zinc Company's Flat Gap mine, Copper Ridge district. Although about 30 airline miles from Jefferson City, these ore bodies are in the same stratigraphic position, but the dip of the bedding averages 37 degrees. Further description of these occurrences would be most welcome.

Believing the evidence of the vug-filling sand to establish the pre-orogeny date of the ore deposition, we looked for alternatives to the customarily cited magmatic-hydrothermal mechanism. In view of the conspicuous sedimentary features and their acknowledged local control of ore emplacement, we hypothesized that the whole process might be syn-diagenetic. This idea was advanced

as a working hypothesis and a basis for further thought and investigation, while recognizing (1, p. 1002) the drawbacks. In the time lag between the first formulation of these ideas and their appearance in print, the biogenetic hypothesis had already been sharply revised and downgraded. Thus, the importance of algae (?) as agents of extraction of zinc from sea water is now largely discounted, not only because of the amount of zinc to be accounted for, but also the very restricted occurrence of algal (?) structures compared to the distribution of zinc sulfide.

Regardless of the mechanism of emplacement of the ore, the evidence of its early emplacement is steadily increasing. In a recent publication (2), Oder and Ricketts state (p. 10–11) that most of the structural features observed in the ore bodies are post-ore in age and that "it appears that the mineralization itself is older than the regional structures which generally are assigned to the post-Paleozoic orogeny." (2, p. 16) While they (2, p. 21) feel that stratigraphic limitation may have been overemphasized, the virtual confinement of this type of ore to pre-Middle Ordovician beds, together with the features of its distribution and mode of occurrence, suggests an Early Ordovician age of the ore deposition.

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LEUCOXENE TERMINOLOGY AND GENESIS

Sir: The contribution entitled "Alteration of Ilmenite" by Lynd (42) concludes with five recommendations "regarding the terminology used and information given in describing work on alteration of titanium minerals." His last recommendation "that the Committee on Publications of the Society of Economic Geologists review the various proposals which have been made regarding the nomenclature of alteration products containing titania, and recommend a uniform system of terminology," or it's early implementation, may be premature in view of various unresolved mineralogical and geochemical problems.

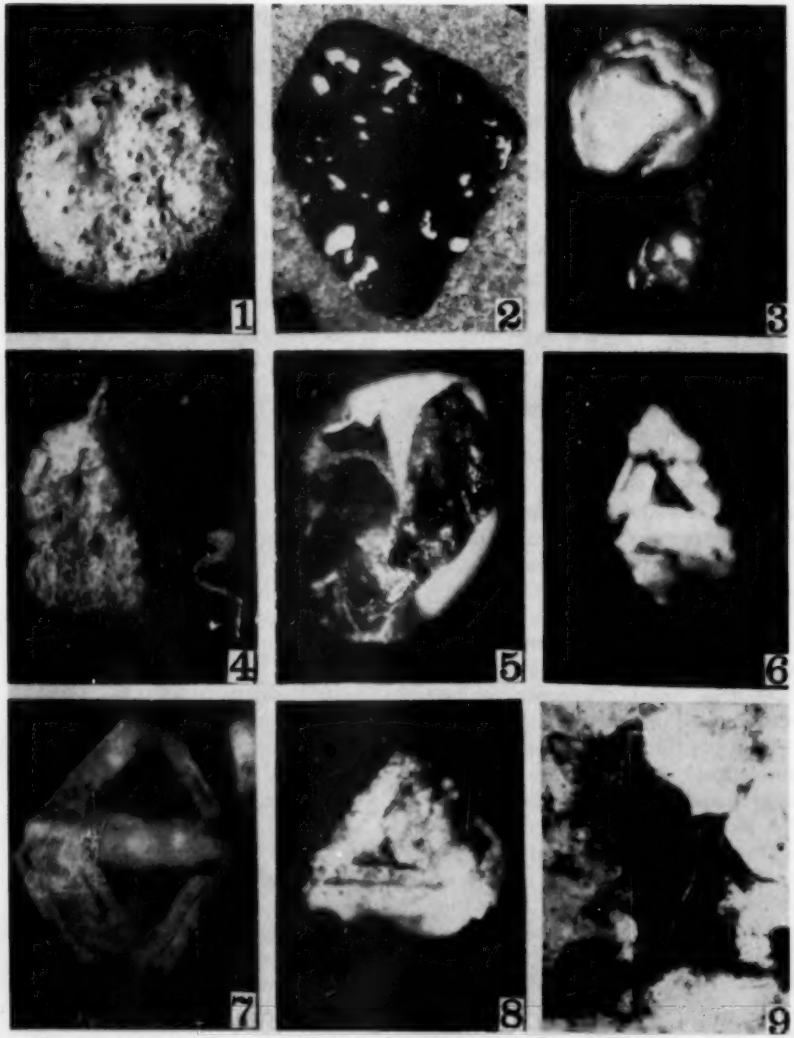
The following comments on the proposals of Lynd and others are based mainly on the present writer's observations on titaniferous constituents of beach sands, clays and consolidated sediments from south-eastern Australia.

Lynd first recommends that "chemical analyses should be given, at least for TiO_2, FeO and Fe_2O_3, on all titaniferous materials studied." This

proposal implies that work on the alteration of titanium minerals is necessarily restricted to minerals and alteration products in which TiO_2, FeO and Fe_2O_3 form the predominant constituents. Many leucoxenic grains from eastern Australian beaches (29) however, contain up to 40 percent quartz per grain as determined micrometrically. Chemical analysis of a handpicked sample of these grains showed: TiO_2, 67.6; SiO_2, 27.6; $FeO + Fe_2O_3$, 1.9; and H_2O, 1.1 percents, respectively, while a diffraction pattern of similar material revealed the presence of rutile, anatase and quartz. Although referred to as "leucoxenic grains" by the writer, such types together with less siliceous grains are classed as "leucoxene" according to local usage.

The tendency for silica to deposit around leucoxene was noted by Scrutton (50, p. 413). In the Australian grains, however, the association is generally more intimate (Figs. 1, 2 and 10). A few grains possibly derive from ilmenite-silicate composite particles since even in ilmenites prepared for analysis Vincent and Phillips (55, p. 19) recorded 0.5, Simpson (51, p. 630, 651), 1.35, and Boulanger (11) up to 2.1 percent silica, respectively. Most grains, however, probably formed by addition of extraneous silica to leucoxene derived from ilmenite (29, p. 226–227 and 31, p. 53), represent pre-existing silica-titania associations such as those described by Frankel (24, p. 177–182) and Williamson (59, p. 27–29 and p. 36–37), or resulted from the alteration of sphene or other silicates such as those listed by Hey (37, p. 97–99). Sphene, a common accessory in hinterland batholiths of eastern Australia, is absent from the beach detritals examined, but its alteration to leucoxene (10, p. 523) and to siliceous and titaniferous products (46 and 32) is recorded elsewhere, and work on the alteration of sphene would require analysis for lime, titania, silica, alumina and other constituents (56, p. 525). Another common accessory in coastal sandstones (31), which contribute to Australian beaches, is a leached biotitic mica densely peppered with a presumably "leucoxenic dust" (Fig. 9), much of which would have a mechanical destination in off-shore clays and silts, but some may have re-aggregated, prior to erosion of the rock, to form larger particles, as observed by Schwartz (49) elsewhere, possibly achieving sand-grade particles of silica-contaminated leucoxene. Since some Australian detrital leucoxenes probably originated at a remote time and place and passed through several sedimentary cycles prior to reaching their present beach location (57, p. 33) the possibilities for derivation are numerous. Many such grains would have failed to resist load stress in contributing rocks (Fig. 4), and transport and beach abrasion, but for early silicification. The numerous constituents recorded by Allen (2) in a "leucoxene" from Roseland, further emphasize the range of products that can occur in "leucoxenes."

Lynd's first proposal might thus be amended to read "chemical analyses should be given to account, at least, for the predominant constituents in all titaniferous materials studied." The difficulty of procuring fractions consisting of identical particles (4 and 16) for analysis, and the possible importance of minor constituents in influencing leucoxenization processes, as indicators of parentage or provenance and in affecting the economic value of the product, e.g., the deleterious chromium in some Australian ilmenite,



Figs. 1, 3, 4, 5, 7, 8 and 9 are reproduced with the permission of the Royal Society of New South Wales.

FIG. 1. Macroporous discoidal siliceous leucoxenic grain from Stradbroke Island dunes, Queensland. Sphericity and rounding are considered to be partly due to colloidal origin. Diameter: 0.3 mm. Inclined incident light.

FIG. 2. Section through a siliceous leucoxenic grain showing about 10% quartz filling macropores. Diameter: 0.3 mm. Transmitted light.

FIG. 3. Colloform, glossy-surfaced leucoxenic pellets showing dehydration cracks that contain quartz. Stradbroke Island dunes. Diameter of larger grain: 0.25 mm. Inclined incident light.

however, should all be borne in mind, and at times will necessitate complete analyses on specially prepared fractions.

Lynd's second recommendation states that the "The term 'ilmenite' should be qualified by the use of an appropriate adjective—e.g., *weathered* ilmenite, when describing the Quilon ilmenite—when it applies to a material other than substantially unaltered, pure ilmenite. Chemical analyses should be used to indicate the degree of purity."

This proposal, like the first, apparently serves to underline omissions in work cited by Lynd elsewhere in his contribution (42) rather than to provide a generally applicable guide in accordance with the stated purpose of the recommendations. Having stressed chemical analysis once, it's re-emphasis to the exclusion of other data could be misleading (20, p. 49–50). The inhomogeneity of many "ilmenites" was partly summarized by Edwards (21, p. 70–77), and Uytenbogaardt (54, p. 184–185). Further observations by Ramdohr (48), Buddington and associates (13), Balsley and Buddington (8), Basta (9) and Katsura and Kushiro (38), indicate that data is still accumulating and considerably less data is available for the alteration products of many ilmenite-spinellid and similar associations, e.g. see Baker (5, 6, 7).

Some Australian detrital grains consist apparently of detrital rutile cores enveloped completely in leucoxene which swells to a central nodule (29, p. 222–223), other rutile grains show a partial filming of leucoxene (Fig. 5). The nature and origin of these grains, which may correlate with rutile-cored ilmenite pebbles from Western Australia (20, p. 53), is uncertain. Some titanomagnetites described by Wilkinson (58, p. 445) were altered internally to deuteric sphene or leucoxene showing "relic structures suggesting its derivation from exsolved lamellae," while spinnelid-like pseu-

FIG. 4. Left: somewhat crushed, partly silica-cemented, macroporous leucoxenic grain. The orientation of macropores may represent former oriented magnetite intergrowths in the original ilmenite or the orientation has been induced by local stresses responsible for the deformation of the grain. Short diameter: 0.15 mm. Lower right: compact leucoxene "schlieren" representing a deformed colloform grain. Both grains in situ in thin section of Hawkesbury (Triassic) sandstone, Sydney district, New South Wales. "Groundmass" is quartz and clay. Inclined incident light.

FIG. 5. Fine-grained leucoxene wrapping round detrital rutile showing internal reflections. Stradbroke Island dunes. Short diameter of grain: 0.2 mm. Inclined incident light.

FIG. 6. Aggregate of pseudomorphs in leucoxene (X-ray indicates anatase) after unknown parent mineral from dike clay, Sydney district, New South Wales. Short diameter of aggregate: 0.12 mm. Inclined incident illumination.

FIG. 7. Hollow, octahedral or dipyramidal pseudomorph in leucoxene (X-ray indicates anatase) after unknown parent mineral or association in dike clay, Sydney district, New South Wales. Short diameter: 0.20 mm.

FIG. 8. Hollow, upper-faced, octahedral pseudomorph in leucoxene (X-ray indicates anatase) after unknown parent mineral in dike clay, Sydney district, New South Wales. Diameter: 0.19 mm.

FIG. 9. Contorted biotitic mica peppered with opaque leucoxenic "dust," in thin section of Hawkesbury sandstone, New South Wales. Transmitted light. Short diameter of mica: 0.3 mm.

domorphs in leucoxene with lamella, hollow and hopper-faced features, from Sydney dike clays (43 and Figs. 6, 7 and 8) are likely to remain puzzling at least until less altered material is encountered. Ores described by Broughton and others (12) ranged from magnetite to "mixtures of titaniferous magnetite, ilmenite, perovskite and leucoxene" and associated rocks contained octahedral leucoxene pseudomorphs possibly after perovskite, some polycrystalline aggregates of leucoxene and other leucoxene showing an imperfect single crystalline character. From the same Uganda district (19) richly leucoxenic-knopite ores have been recorded. These examples suggest that Lynd's second proposal oversimplifies a complex problem. Chemical, micrographic, X-ray and other data are necessary to characterize "ilmenites" and all other titaniferous materials.

In his third proposal Lynd deplores the introduction of new terms, or the revival of old, little known, or discredited terms to designate alteration products of titanium minerals "since all of these materials can be covered by the term 'leucoxene' which is in current use." While some discussion may arise as to what constitutes a titanium mineral, the common occurrence of ilmenite-spinellid and other intergrowths suggests that many oxide associations be included in any consideration of titanium minerals and their alteration. If this is agreed it becomes necessary to consider such alteration products as titanomaghemite (38), associations of pseudobrookite and hematite probably derived from titanomagnetite and ilmenite (41) and various "hydroilmenitic" (22 and 23) and "arizonitic" (40) products, in addition to many other types of titaniferous alteration product. Pending further clarification on the nature and derivation of these products there may be some justification for the retention of some old terms, preferably used adjectivally (e.g., "arizonitic" rather than "arizonite"), and further work may well suggest the introduction of several new terms for the useful characterization of the alteration products of titanium minerals.

Lynd fourthly recommends that the term " 'leucoxene' should continue to be used as a general name for alteration products containing titania." This is a variant of Allen's (2) recommended use of "leucoxene" "as a petrographic term for the alteration product in which titania occurs in rocks," and Bailey and Camerons' (4) proposed modification of Allen's usage so that it reads ". . . for any alteration product in which titania occurs in rocks," although for mineragraphic purposes they prefer to limit the term to crystalline TiO_2. In the present writer's view all of these proposed usages should be rejected on the following grounds: Firstly: "alteration products containing titania include many bauxites, laterites, clays, cherts and similar materials but the identity of these materials with "leucoxene" is unacceptable. Secondly: some bauxites and clays examined by the writer contain titania present as single crystal detrital rutile of silt- to sand-grade dimensions, in which case neither the host material nor it's included titania is acceptable as "leucoxene." Thirdly: among the "alteration products in which titania occurs in rocks" we might legitimately include silt- to sand-grade single crystal particles of secondary sphene (14, p. 352), ilmenite (25, p. 90), titanomagnetite (45), titanomaghemite (38), pseudobrookite (?) (41, p.

679), anatase (31, p. 49), and brookite (33) and the identity of all these products with leucoxene is unacceptable on the grounds of particle size and diversity of crystal structure if not because of compositional diversity. Nor can the present writer agree that leucoxene should have differing petrographic and mineragraphic connotations.

Lynd proceeds in his fourth proposal to recommend the use of one or two adjectives to indicate the degree of crystallinity, color and crystalline phase present. Perusal of Figure 10 indicates, however, that the categories "crystalline" and "amorphous" do not sufficiently characterize given leucoxenic grains. Bailey and Cameron (4) moreover found 24 biphasal grains

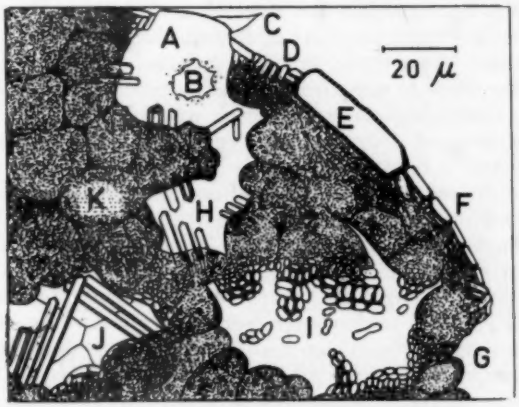


FIG. 10. Schematic drawing of portion of a thin section of a siliceous leucoxenic sand grain from Stradbroke Island, Australia. A. Quartz, largely filling macropore. B. Unfilled remnant of original macropore. C. Outgrowth of quartz. D. Surface of grain showing randomly oriented microlites. E. Rutile "inclusion" presumably resulting from aggregation of microlites locally. F. Portion of surface with tangentially oriented microlites. G. Gouge pit or unfilled macropore at grain surface. H. Rutile microlites developed at former free surfaces and projecting into now quartz-filled macropores. I. Anatase (?) microlites showing growth toward free surfaces bounding macropore. Some microlites were detached and trapped by silica during cementation. J. Polygranular grain contacts of quartz in macropore cement. K. Sub-grain of opaque to cryptocrystalline "leucoxenic substance." Bulk of grain is composed of these ill-defined ovoid sub-grains.

in 100 examined and Karkhanavala and others (39) noted up to 4 crystalline phases in some leucoxene fractions. Bailey and Cameron (4) also found that microlite orientation varied for different phases within single grains. Color, in conjunction with grain morphology and physical properties, was useful as a rough classification of Stradbroke Island dune-sand leucoxenic grains (29) which were grouped into: I: magnetic ilmenite-leucoxene composites, II: Non-magnetic "white opaques," which, however, included white, cream, yellow, gray and some brown grains, and which were subdivided into IIa: macroporous leucoxene-quartz aggregates (Figs. 1, 2), IIb: mat-surfaced

grains and IIc: glossy-surfaced colloform pellets (Fig. 3), III: Non-magnetic amber-like grains, which graded into imperfect single crystals of sand-grade rutile and also into types IIb and IIc, and IV: non-magnetic rutile-leucoxene composites (e.g., Fig. 5). All types other than IIa still await study, but for this type, the dominant one, morphology, texture, density, grain and powder optics, solubility, chemical and X-ray data were obtained on hand-picked samples. However since no two grains were identical this study must still be considered as a reconnaissance on a small sample.

In contrast to Lynd's views Flinter, although conceding (22) that complete leaching of iron from ilmenite is theoretically possible, maintains (23) that iron oxides are a "fundamental component of the end product of ilmenite alteration" and further that the term "leucoxene" should on no account be used for the alteration products of ilmenite since leucoxene is "pure TiO_2" and is derived "from rutile, brookite, anatase, sphene or similar material." Although the white to pale cream alteration product of ilmenite has probably never been irrefutably analyzed, since it would be necessary to remove such films from attached ilmenite while ensuring freedom from ilmenite contamination, and at the same time to be certain that the light colored material was in fact derived from ilmenite and not from former attached rutile, etc., nevertheless Flinter's views seem to the writer to conflict with general petrographic experience and common usage. Further, with the exception of the alteration of sphene and probably of ferroan rutile to leucoxene the leucoxenization of the other phases referred to is doubtful. On the contrary, the theoretically expected tendency for decrease in the surface area of leucoxenic systems, as implied by Tyler and Marsden, has since been verified by numerous occurrences of the growth of rutile and anatase (29 and 31) and brookite (33) at the expense of leucoxene. Not only does the alteration of some ilmenite to ferriferous products fail to justify the generalization made but "pure" leucoxene also should not be regarded as an unqualified "end product" of ilmenite or any other alteration, for despite its "stability" in the usage of sedimentary petrology, the instability of leucoxene, especially during its formative stages, is similar to that of other mineraloids, the tendency toward single crystal development seldom being achieved over whole aggregate dimensions, but renewed growth occurs during appropriate diagenetic, hydatogenetic and metamorphic conditions. It is for this reason that a term such as "leucoxenic anatase" is ambiguous since it might imply single crystal silt- to sand-grade anatase outgrowths from, or replacement of, leucoxene, or anatase of leucoxenic dimensions. Use of the reverse terminalagy, e.g., "anatasic leucoxene" also requires caution since, as remarked by Allen (2) a small amount of crystalline within amorphous material may give misleading X-ray results.

In the writer's experience much leucoxene is characterized by a limited although broad range of chemical, petrogenetic, micrographic, morphologic and physical attributes and the fullest data covering all these attributes is desirable for every sample and occurrence examined. Apart from a high titania content, derivation from pre-existing minerals usually containing three or more essential elements, and an occurrence in aggregates of fine particle

size, generalizations are difficult, but pending the accumulation of data, the writer would limit use of the unqualified term to material containing at least 75 percent TiO_2, and consisting predominantly, say 90 percent by volume, of particles having a maximum short diameter of 5 microns. The term "high titania leucoxene" might also be used for such material. For material containing less titania or/and more coarse particles it seems advisable to refer to "ferriferous-," "siliceous-" or otherwise qualified leucoxene, or "leucoxenic" or "titaniferous" materials, or to "composites" or "aggregates" appropriately qualified. Whenever adequate compositional and dimensional data is lacking it also seems desirable to replace the substantive by a broader term such as "leucoxenic" grains or material. Where locally applicable, practical classifications, usages or compositions might be indicated diagram-

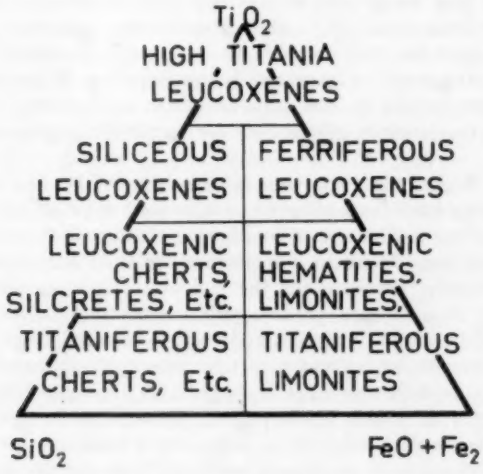


FIG. 11. A possible initial classification and terminology, of local applicability, for some detrital leucoxenic grains in south eastern Australia.

matically, as in Figure 11, it being understood that such a scheme has no petrogenetic significance and no general application. With increasing numbers of plus 5-micron particles demarcation problems of terminology, as with sandy shales and shaly silt-stones are inevitable.

A satisfactory terminology is unlikely to emerge until the lineages of various leucoxenic materials have been traced, and more is known concerning leucoxenization processes. As visualized by the writer, the latter usually imply decomposition and differentiation under weathering, deuteric or hydrothermal conditions. To weathering factors such as environmental hydrology, pH and Eh, time, and the ionic potentials of the ions involved, others such as crystal structure and particle sizes of the parent minerals, which influence accessibility of fluids to the bonding and soluble cations, and inhomogeneity

within parent minerals, which probably influences thresholds, rates and products of leucoxenization, should also be considered. While some products are removed in solution or suspension to be precipitated elsewhere, others form a precipitate, paste or gel, contaminated by entrapped material, which replaces the parent mineral.

Some Australian coastal rocks containing variously leucoxenized ilmenites, partly inherited from older sediments, display alternating thin laminae of varying permeability (28) within which further, but differential, leucoxenization probably occurred. Erosion of these beds provided a polygenetic series of leucoxenized products which mixed with other series and were subjected, for varying periods, to saline, intertidal conditions alternating with dune episodes involving other pH and Eh conditions. In some dune swamps grains became coated with iron-oxides mixed with organic matter and some diffusion of ions into the crystal lattice may have occurred (30), in others titania may have been added (15) or leucoxenization advanced (3). Older leucoxenization episodes may be wholly or partly obscured by microlite growth and superimposed or repeated leucoxenization of grains may have occurred. Several orders of diversity are thus represented by leucoxenic detritals and the mechanisms responsible for particular grains are frequently obscure.

The role of supergene processes is also frequently in doubt because leucoxenization may have been initiated or advanced in prior hypogene conditions. During a "normal" range of weathering conditions removal of ferrous iron from ilmenite may result in a transitory colloidal suspension of titania in situ. Alternatively, evidence for the colloidal origin of some leucoxene (29) may point to a silicate parent. Leucoxenization of titanomagnetite in the acid leached zone at Wairakei (53) either resulted from a more "aggressive" environment or indicates a titanomagnetite-ilmenite, -ulvospinel or similar parental associations since homogeneous titanmagnetites apparently alter to titanomaghemites as a result of both deuteric and weathering conditions, without leucoxenization (38). Ilmenites containing spinnelid inclusions other than ulvospinels or titanium-rich titanomagnetites might thus be expected to alter to relatively ferriferous leucoxenes as compared with purer ilmenites altering under the same conditions. A converse relation to that usual in weathering, with removal of titania to leave enriched iron deposits, was attributed by Mann (44, p. 252, 272) to "mildly alkaline hydrothermal solutions acting upon silicated iron formation for a long period of time." Irrespective of mechanism, the precipitation of such mobilized titania might account for its occurrence in residual sediments derived from rocks lacking titania (I, p. 143–4), the local accretion of globules of such titania could also account for the colloform pellets, and deposition of such titania on rutile surfaces might explain some of the other associations, present in Australian sands.

For the leucoxene in "greenstones" and similar low-grade metamorphic rocks, the roles of "metamorphic metasomatism" and prior leucoxenization in parental rocks, is again in doubt. Simpson (52, p. 71–3) recorded replacement of both ilmenite and leucoxene by pyrite, but Derry (17, p. 921) and

Gruner (34) ascribed some leucoxene to sulphurization of titaniferous magnetite, and of ilmenite, respectively.

In addition to a range of hydatogenetic and possibly pneumatolytic environments favoring leucoxenization, other processes such as recrystallization of metamict products and devitrification of the fulguritic fusion products of rutillic and ilmenitic sands possibly merit consideration. Numerous fulgurites collected by the writer on dunes adjacent to Australian black sand deposits show partial fusion of rutile and ilmenite and diffusion of the brownish glass into the lechatelierite.

At times crystal growth following leucoxenization was probably accompanied by additive reconstitution to sphene and titanic iron oxides. Replacement of sphene by ilmenite (25, p. 90), of sphene by titanomagnetite (45), of titaniferous iron oxides by sphene (14, p. 352) and of rutile and sphene by ilmenite (56, p. 67, 526) and similar transformations, where partially completed, could, as a result of subsequent leucoxenization, account for some of the detrital associations observed. Such transformations also may have involved transitory leucoxenic stages, as also may the "type 2" alteration of ilmenite to optically identifiable anatase noted by Hartman (36, p. 1403). These transformations and the proposed origin of various titanic ore bodies as late magmatic (27 and 35), pneumatolytic (26) and by progressive (47) and retrogressive (18) metamorphism, render the terms "primary" and "secondary" of doubtful connotation as applied to titanium minerals. Leucoxene, however, seems to be a generally metastable system appearing at various locales in the cycle of titanium as a result of breakdown or transition of pre-existing solids.

Titanium, the ninth most abundant crustal element, apparently fails to achieve high grade sedimentary geochemical differentiates other than resistate accumulations, and thus contrasts not only with the more abundant elements but also with manganese and phosphorus. If ilmenite grains weather to a high titania leucoxene the same process might have been expected to manifest itself for some ilmenitic ore bodies unless unfavorable permeability, or location, of ore has inhibited leucoxenization, inadequate prospecting has failed to reveal it, or former deposits have been dispersed by glaciation or tectonism.

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BRECCIA AND PEBBLE COLUMNS ASSOCIATED WITH EPIGENETIC ORE DEPOSITS

Sir: In Vol. 56, page 488 of this Journal, Leonid Bryner presents a review paper of considerable interest. I wish to take exception to some of his interpretations.

On page 489, he says, "Emphasis is placed on those breccia and pebble structures that show the most direct relationship to ore deposition and which appear to be an outgrowth of hydrothermal activity." This group of breccia and pebble structures is referred to an "co-hydrothermal."

The assumption is made that so-called "co-hydrothermal" breccia and pebble columns are genetically related to hydrothermal solutions. The references are to published works so describing such deposits, yet there seems

little reason for making such a broad separation as is attempted in this paper.

The author restricts his discussion to those formed as a result of hydrothermal activity. As hydrothermal activity is generally regarded as a feature of magmatic-action, I conclude that his "co-hydrothermal" breccia and pebble columns are related to magmatic action.

As his "pre-hydrothermal" pipes are features of magmatic action, either intrusive or volcanic, it appears that the separation is arbitrary and undesirable.

It is only natural that the literature should be replete with descriptions of mineralized breccia columns and pipes. Yet the features described as diagnostic of breccia pipes formed by hydrothermal action are equally diagnostic of volcanic collapse features. It appears that what is being described may be the results of hydrothermal alteration and mineralization of pipes and columns formed by magmatic processes, either hypabyssal or volcanic.

So far as I know, there is no geological reason why magmatic processes of intrusion and extrusion should not be occurring while mineralization processes are in progress at different points in the magma mass. Cycles of mineralization followed by new intrusive cycles have been observed, indicating variations in the products of the magma at different times.

The concept of mineralization stoping as a general means of formation of breccia pipes has always seemed far-fetched to me. Unless physical connection with the surface is indicated, the problem of disposal of the dissolved material has appeared insurmountable. On the other hand, the concept certainly has merit in consideration of those deposits in the epithermal zones where corrosion of traversed formations may result in re-deposition of the dissolved material at the surface. Collapse might be present in such a case but development of a pipe such as the Bull Domingo as described by Peters would seem more likely.

The author applies the term "co-hydrothermal" because brecciation appears to have been more or less contemporaneous and coextensive with mineralization and is interpreted as an effect of the mineralizing fluids themselves. A volcanic environment commonly is absent or, if present, shows no spatial relationship with the pipes.

Lack of a volcanic environment, as such, can hardly be used as the basis for relating breccia pipes to hydrothermal solutions, as many barren breccia pipes, similar to those of volcanic type, are known in many areas where no volcanic environment exists. A parallel might be drawn by stating that hydrothermal solutions are not related to a magma because no magma is known in an area.

Although this is a very interesting paper, and the bibliography is impressive, I believe that introduction of the word "co-hydrothermal" is unnecessary and undesirable. Although mineralized breccia columns may conceivably have been formed through hydrothermal action along veins or other structures, it appears more likely that most are related to volcanic or hypabyssal activities.

W. J. WALKER

REDDING, CALIFORNIA,
Aug. 1, 1961

Economic Geology
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REVIEWS

SHORT REVIEWS OF NEW RUSSIAN BOOKS

Angaro-Ilimskie zhelezorudnye mestorozhdeniya. [The Angaro-Ilimskie iron-ore deposits.] Edited by G. B. CHERNYSHEV. Pp. 376; figs. 79. Gosgeoltekhizdat, Moscow, 1960. Price, 25r. 40k.

The Angaro-Ilimskie iron-ore field comprises 18 deposits in volcanic necks associated with the trap formations of the southern part of the Siberian platform, and contains reserves of 1284 million tons of magnetite ore ranging 30–56 percent iron. The Korshunovsk, Rudnogorsk, and Krasnoyarsk ore-bodies are the most important. All the ore is low in titanium (about 0.3% TiO_2). The volcanic necks, pipe-like in form and ellipsoidal in plan, extend up to 2400 × 700 meters in surface area. They are filled by breccias and agglomerates consisting dominantly of basaltic and doleritic tuffs, bombs, and lapilli, which range in particle size from a few millimeters up to 10–15 cm. Fragments of argillite, sandstone, marl and limestone disrupted from the strata underlying the traps are also present. These sedimentary components are mostly of Upper Cambrian to Lower Silurian age, though in some pipes xenoliths of coal and other sediments from Lower Permian formations are found. The probable age of the tuffs is Triassic or Jurassic, contemporaneous with the Siberian traps; but one vent carries xenoliths with an Upper Purassic-Lower Cretaceous fauna, suggesting that the volcanic period was long continued. Ores are present mostly as vein or lode formations of magnetite or martite, bearing a high iron content (up to 67%), from 0.5 to 40 meters in width, with sharp margins to the ventagglomerates that they traverse, and dipping irregularly from near vertical to near horizontal. In texture this magnetite mineralization varies greatly, but oolitic, spherulitic, and other collomorphic developments are particularly prevalent. Less rich metasomatic magnetite ores (15–50% iron) take the form of garnet-pyroxene skarns replacing pyroclastic tuffs and xenolithic marls and limestones. The ore reserves have been proven by drilling and drifting, and the pipe breccias have been found by drilling to persist to minimum depths of 200–700 meters. It is believed that the ore-bearing solutions have been derived as late differentiates from the trap magma. Locally they have caused chloritization, zeolitization, and carbonatization of the breccias. Apparently the occurrences are unlike any other major deposits recorded in geological literature.

Geologiya svintzovo-tzinkovykh mestorozhdenii Primor'ya. [Geology of the lead-zinc deposits of Primor'ye.] By E. A. RADKEVICH and others. Trans. Institute for the Geology of Ore Deposits, No. 34. Pp. 328; figs. 109. Academy of Sciences, Moscow, 1960. Price, 17r. 70k.

In the post-war years the exploration of the Pacific Maritimes (Primor'ye) has resulted in the discovery of ore fields of great importance, and it is significant that a conference on the Pacific ore belt held in Vladivostock last October attracted 400 geologists from 62 organizations. The present work is the first book of a multi-volume publication on the geology of the lead-zinc deposits of the U.S.S.R.,

and it is in large part concerned with studies on the Ol'ga-Tetyukhinsk metalliferous region in the Sikhote Alin. The Primor'ye ore province is part of the Pacific metalliferous belt characterized by a widespread development of tin mineralization, and lead-zinc ores rank subordinately to tin. They form independent bodies only at a few localities, as galena-sphalerite-fluorite veins of relatively small size, and most of the metallization occurs as polymetallic skarn and vein deposits of cassiterite-sulphide type. The memoir presents a well-documented and clearly presented account of the general geology, with detailed studies of the principal ore occurrences, but it is much too long to summarize in a brief notice.

Struktury rudnykh polei i mestorozhdenii. [The structure of ore fields and ore deposits.] By F. I. Vol'fson, L. I. Lukin, and others. 624 pp. Gosgeoltekhizdat, Moscow, 1960. Price 40r. 15k.

A lengthy collective work by 25 authors is divided into two parts, the first of which (pp. 15–394) is concerned with the application of geological and geophysical mapping to the study of ore deposits, special weight being given to techniques of tectonic analysis. Most of this is text-book material drawn both from Russian and Western literature. Perhaps a greater interest resides in the second part of the book (pp. 397–621) which gives examples of structural researches in the investigation of Russian orefields. These include papers on the Tzaginsk gabbro-anorthosite complex (Kola peninsula) with titanomagnetite deposits; the Slyudyanka phlogopite deposits near Lake Baikal; various molybdenite and wolframite deposits in eastern Transbaikalia; magnetite ore-bodies associated with the Siberian traps in the Tunguska syncline; the Turinsk copper skarns in the eastern middle Urals; the Shamlugsk sulphide ores of Armenia, principally massive pyrite-chalcopyrite-sphalerite deposits in tuffs; the Kurgan polymetallic field (Kirgizia), with geothermally zoned cassiterite-sulphide veins around a syenite intrusion; the Smirnovsk chimneys of galena-sphalerite ore in Lower Palaeozoic limestones and dolomites (eastern Transbaikalia) and somewhat similar polymetallic pipes of the Ekaterino-Blagodat field in the middle Urals; the Emeinogorsk gold-polymetallic ore-bodies of the Rudnyi Altai forming microquartzite-albitophyre lenses in argillites; the Dolpran goldfield in the Tyan Shan, exhibiting a group of hydrothermal veins in pre-Cambrian gneisses and schists intruded by Caledonian granites; and the important Baleisk goldfield in the Chitinsk oblast of R.S.F.S.R., where a complicated system of auriferous quartz-chalcedony-adularia-kaolinite veins (with pyrargyrite) has formed contemporaneously with the development of graben in Mesozoic sediments. All of these contributions are succinct and clearly written, eminently suitable for translation.

Tallii. [Thallium.] By V. V. Ivanov and others. Pp. 156. Academy of Sciences, Moscow, 1960. Price 7r. 15k.

Gallii. [Gallium.] By O. V. Vershkovskaya and others. Pp. 146. Academy of Sciences, Moscow, 1960. Price 6r.

These two small handbooks, similar in format, have been produced by the Institue for the Mineralogy and Geochemistry of the Rare Elements, under the direction of K. A. Vlasov. They give a comprehensive review of the economic geology, geochemistry and mineralogy of the two elements, with a long bibliography in each case. Although based largely on published Russian and Western literature, a great many new spectrographic analyses are given to demonstrate the gallium content of various minerals (with acknowledgements to some 40 of the

Institute's analysts!) and much new information is contained in a chapter on the geochemical provinces of thallium throughout the U.S.S.R. Notwithstanding the small commercial interest of these rare elements, the amount of recent data concerning them is quite spectacular.

Geologicheskii slovar. [Geological dictionary.] By A. N. KRISHTOFICH and others. Vol. I, pp. 402, vol. II, pp. 445. Gosgeoltekhizdat, Moscow, 1960. Price (two vols.) 53r. 20k. [£4.].

This is a reprint with minor corrections of the very useful glossary of geological and allied terms first published in 1955 (long out of print) and reviewed in ECONOMIC GEOLOGY, 1959, pp. 336–7. The total printing has now been 55,000 copies. Unfortunately although the price in Moscow remains the same as that of the first edition, the price in London has almost doubled.

Kratkaya geograficheskaya entziklopediya. [Short geographical encyclopaedia.] Chief Editor, A. A. GRIGOR'EV. In four volumes. Vol. I, pp. 563, figs. 386, with 131 maps in text and 24 colored maps. Sovetskaya Entziklopediya, Moscow, 1960. Price, 35r. per volume.

One of the many difficulties confronting the average Western student of Russian geological literature is his lack of knowledge of the geography of the remoter parts of the U.S.S.R. This well produced quarto reference work should help to remedy this, for although it covers the world it naturally gives fullest attention to the Soviet Union. According to the preface in volume one (A–D), the four volumes will include 16,000 separate articles (alphabetically arranged and ranging in size from a few lines to several pages), among them 3,500 on general questions such as topics in physical and botanical geography and 11,000 on the regional geography of the Soviet Union and foreign countries. In all there will be 130 colored maps, 400 text-maps, and some 1,200 other illustrations. Volume IV will also provide 400 articles on the peoples of the world, with around 1,000 biographical entries on explorers and other geographical pioneers. No other encyclopaedia has a comparable content, and the work should prove a useful acquisition in any library concerned with the earth sciences.

Geologiya olovonosnykh mestorozhdenii Severo-Vostoka SSSR. [Geology of the tin deposits of North-East U.S.S.S.R.] By V. K. CHAIKOVSKII. Pp. 335 + 3 maps. Gosgeoltekhizdat, Moscow, 1960. Price 15r. 40k.

Some 25 years ago tinstone was discovered almost simultaneously in the western Verkhoyansk, Chaun-Chukhotsk, Kolyma, and Alak-Yunsk districts of north-eastern U.S.S.R., since when an extensive prospecting campaign has reputedly demonstrated that the region is one of the largest stanniferous provinces in the world, claimed to extend over an area of 2,500,000 square kilometers. Whilst various other metals such as cobalt may prove to be of local interest, the tin, wolfram and gold of this region are of All-Union significance. The memoir, which presents the first reasonably full description of these deposits, is divided into three sections respectively on the regional geology, on the geology of the individual deposits, and on the processes of metallization—the last being a thoughtful contribution of unusual interest. Three phases of mineralization are recognized, designated as late Kimmerian, Lower Cretaceous and Laramide, all forming part of the same long-continued tectono-magmatic cycle but each having its characteristic features. Most of the gold-quartz mineralization is related to the first phase, minor polymetallic

deposits with small quantities of tin and wolfram to the second, and the main commercial tin-wolfram deposits, with polymetals, to the third. Not a word is said about the climatic conditions, which are perhaps the most severe on earth; but it is small wonder that popular paper-backs have recently appeared in Russia in praise of the work of the tin-field geologists.

C. F. DAVIDSON

UNIVERSITY OF ST. ANDREWS,
SCOTLAND,
20th April, 1961

Geologic Map of California, Olaf P. Jenkins Edition. Death Valley sheet, by CHARLES W. JENNINGS; Alturas sheet, by THOMAS E. GAY, JR., and QUINTIN A. AUNE; San Luis Obispo sheet, by CHARLES W. JENNINGS; Santa Cruz sheet, by CHARLES W. JENNINGS and RUDOLPH G. STRAND; Santa Maria sheet, by CHARLES W. JENNINGS; Westwood sheet, by PHILIP A. LYDON, THOMAS E. GAY, JR., and CHARLES W. JENNINGS. Each sheet accompanied by complete explanation, chart of stratigraphic units, topographic quadrangle index map, index chart and references to sources of geologic data, and photographs. California Division of Mines, 1958–60. Price, $1.50 per sheet.

The new geologic map of California represents the most ambitious effort of its kind thus far undertaken by a state organization. Conceived by Olaf P. Jenkins, (now retired), this project has gained momentum under the direction of his successors, Gordon B. Oakeshott and Ian Campbell. The final product, to appear in the form of nearly thirty separate sheets at a scale of 1:250,000, will supplant the state geologic map published in 1938 (scale 1:500,000) and out of print since 1952.

The first units of the new map were issued in 1955 as eight preliminary sheets, printed in black on white, that cover much of the coastal and interior desert regions of southern California. Then compilation was mainly the responsibility of Charles J. Kundert, who encountered serious difficulties in adjusting the geologic data to the generalized topographic base maps then available. Although this preliminary edition was well received, no attempt was made to complete it because superior new base maps were being prepared. Products of an Army Map Service program of upgrading the topographic map for the state, these 1:250,000-scale sheets are being compiled from modern quadrangle maps and air photographs. They include up-to-date cultural and land-net data, with improved topographic expression. Contours, spaced at 500 feet on the earlier maps, are now refined to a 200-foot interval and are supplemented in some areas by 100-foot contours. Offshore topography is shown on the coastal sheets by means of 300-foot contours. Each sheet normally encompasses an area one degree of latitude by two degrees of longitude.

Compilation and recompilation of geologic data on the new topographic base for the final colored edition of the state map has progressed rapidly during the past five years, in large part through the efforts of Charles W. Jennings. Six of the final sheets have been printed thus far, and coverage for the entire state should be at hand within a few years. The published sheets represent three geographically separated regions of highly contrasting geology, and hence provide a good sampling of what is to come.

These maps are unusually attractive in general appearance. They are easily read despite the enormous amount of detailed information they contain, thanks to careful plotting of geologic boundaries with respect to topography, the use of

fine-line scribing techniques in preparing the copy, and the judicious combining of various patterns with pleasing colors. The printing is clean and in good register. Proofing the sheets must have been a nightmarish task, but it has been well done; detailed search will reveal only a few cartographic infelicities (e.g., geologic contacts crossing faults without apparent offset, small patches of ground that cannot be identified geologically, contacts that don't match across map boundaries). The published sheets reflect adherence to the announced policy of integrating the entire project "so that adjacent sheets will match in continuity of geologic units, color, and scale, insuring that adjacent sheets can be trimmed and joined if desired." It is evident that the colors of some units do not and will not match across several boundaries between sheets, but this is hardly a serious matter because reasonable continuity is provided by patterns and contacts that with few exceptions do match, and by an adequate distribution of symbols on all the maps.

A geologic legend for the entire state is a part of each map sheet, and those units appearing within a given sheet are indicated by a heavy border on each of the corresponding boxes in the legend. The master legend comprises 79 units designated by separate colors and/or patterns, along with an additional 39 units distinguished by special symbols. Known and inferred faults are clearly shown, and most of the major breaks are designated by name. Also identified on the maps are other prominent geologic features not included in the legend (e.g., dacite domes, calcareous tufa mounds, Wildrose graben).

The choice of units for state-wide coverage on the final geologic map reflects in various ways the extreme lithologic and temporal diversity of the California section, the close association of marine and nonmarine sedimentary sequences in many areas, the occurrence of sedimentary rocks and their metamorphosed equivalents in adjacent regions, and the presence in some areas of numerous distinguishable but closely related units that represent relatively short intervals of geologic time. To delineate these and other significant relationships, within the limitations of map scale and information available, has required some unusual subdivisions of the section and the abandonment of all formal names save Knoxville and Franciscan. Primary classification still is made according to age, but environment and genesis form the chief supplementary basis for dividing Quaternary deposits (12 units), marine or nonmarine origin for dividing the sedimentary rocks (39 units), and modal composition for dividing the volcanic rocks (33 units). For example, the alluvium in the Sacramento-San Joaquin Valley is subdivided into stream channel deposits, fan deposits, and basin deposits, and the Pleistocene volcanic section on the Modoc Plateau is subdivided into rhyolite, andesite, basalt, and pyroclastic rocks.

Imaginative combination of routine with unconventional techniques of presentation has yielded map sheets that do real justice to known lithologic, structural, environmental, and regional relationships. Criticism of some things that are shown (and some that are not) can be anticipated, but such criticism must reflect far more upon the present state of geologic understanding than upon the maps themselves. Numerous unsolved problems are indicated or implied on the maps and accompanying stratigraphic charts, and marked differences in detail of basic data can be seen or sensed from the maps, charts, and index diagrams.

Areas perforce marked as "unmapped" or "incomplete" amount to very small percentages of some sheets and are absent entirely from others. This impressive improvement over the previous edition of the state map is attributable not only to the inclusion of useful information published since 1938, but also to numerous contributions of unpublished data by state and federal agencies, universities and

colleges, private corporations, and by many individuals. Significant additions have been made through a program of reconnaissance mapping recently established by the State Division of Mines in a further effort to eliminate "blank" areas from the new map. It also seems clear that the era of individual ground coverer has not yet come to a close; a glance at the index diagrams showing sources of data gives evidence, which will become increasingly eloquent as more sheets are published, of the remarkable field activities of T. W. Dibble, Jr., who certainly must qualify as California's modern-day Darton!

All participants in this massive project, from the staff of the State Division of Mines to that of Williams and Heintz Lithograph Corporation, deserve warm thanks and congratulations for the excellence of the products thus far published. Both these and the final map should be of great value to a wide spectrum of users for many years to come.

RICHARD H. JAHNS

DIVISION OF EARTH SCIENCES,
THE PENNSYLVANIA STATE UNIVERSITY,
UNIVERSITY PARK, PENNSYLVANIA,
July 12, 1961

Geology of Ore Deposits (Geologiya Rudnykh Mestorozhdenii). Academy of Sciences of the USSR. November–December, 1959; Vol. 1, No. 6 (in Russian).[1]

A. G. BETEKHTIN, G. A. SOKOLOV, *The sixtieth birthday of academician D. S. Korzhinsky*[2] (pp. 3–4).

Dmitry Sergeyevich Korzhinsky made extensive contributions to the theory of metasomatic processes, particularly to the study of metasomatic zoning and paragenesis of mineral formations under specific geological conditions. The subject of his latest studies was the interaction of the mineralizing solutions with the enclosing rocks. Of great interest are his investigations of the mutual influence of the components' potentials in the solutions. Korzhinsky is one of the most experienced Russian field geologists and combines his studies with thorough analyses based on thermodynamics.

A. G. BETEKHTIN, *The exogenetic processes in the formation of uranium deposits* (pp. 5–26).

The most characteristic geochemical feature of uranium is its capacity to form under oxidizing conditions the complex cation $(UO_2)^{2+}$ which in turn forms hydrous compounds with other ions. Uranyl is easily adsorbed by all kinds of gels, finely dispersed minerals, and organic compounds. The most soluble uranyl compounds forming in the zone of oxidation are the sulfates, which are followed by carbonates, hydroxides, arsenates, vanadates, phosphates, and hydrosilicates, the last being the least soluble. The sulfates and uranyl carbonates form under similar conditions. Hydroxides and uranium hydrates form on the surface of carbonate and pitchblende veinlets, when the supergene solutions are deficient in anions with which uranyl forms salts. In general, the hydrosilicates, and especially phosphates, with some arsenates, are paragenetically younger than the hydroxides. The uranyl vanadates in the deposit of Tyuyamyun probably formed during the oxidation of primary hydrothermal deposits. Referring to the Colo-

[1] Regular preparation of reviews of this journal is supported by a grant from the National Science Foundation.

[2] On September 13, 1959.

rado Plateau, Betekhtin indicates that the uranium- and vanadium-bearing horizons above the water table represent a gigantic zone of oxidation accompanied by some migration and redeposition of ore minerals. Uranium deposits of economic value form in the zone of cementation. However, during the weathering of uranium deposits and uranium-bearing rocks, the major part of uranium is carried away.

Besides the zone of oxidation, the exogenous deposits are represented by: (1) placers, (a) alluvial, (b) marine and dune placers; (2) syngenetic deposits, (a) in conglomerates and sandstones, (b) in argillaceous deposits, (c) in marls, argillaceous limestones and phosphorites, (d) in caustobioliths; (3) epigenetic deposits, (a) in sandstones and conglomerates, (b) in caustobioliths; and (4) metamorphic deposits. Conditions of deposition are reviewed from sedimentalogical and physicochemical points of view. The author stresses that there is some similarity in the formation of sedimentary uranium deposits with the deposition of iron and manganese ores and phosphates. A sedimentary origin is supported for pitchblende and pyrite in deposits of Witwatersrand and Blind River.

The exogenous uranium deposits, including the metamorphic deposits, are of low grade, but their potential reserves are extensive. It seems that the Soviet uranium industry is primarily interested in this type of deposits.

V. I. Danchev, A. M. Kornilov, M. V. Neimyshev, V. V. Ol'kha, B. K. Proshlyakov, N. P. Strelyanov, M. P. Sytnikov, *Uranium mineralization in sedimentary carbonate rocks* (pp. 27–38).

The uranium deposit is associated with carbonate rocks of Lower Tertiary age. Most uranium occurs in oolitic limestone and in limestones of organic origin. The abundance of organic matter in these deposits results in accumulation of iron sulfides which give the rock a black color. The elements that accompany uranium are: V, Mo, Pb, Ni, Co, Cu, Se, Bi, and Cr. The primary ores mostly consist of sooty pitchblende and pitchblende, which are accompanied by pyrite, marcasite, some galena, sphalerite, chalcopyrite, and molybdenite.

The accumulation of uranium occurred in the transition zone between the oxidizing near-shore marine facies and the reducing facies. This coincided with the accumulation of calcareous oozes. The slow rate of predominantly chemical sedimentation evidently created conditions favorable for the sorption of uranium by organic matter. Local depressions of the sea bottom were especially favorable for the accumulation of uranium in a pelitic fraction of the sediment (< 0.01 mm). The uranium-bearing rocks are saturated with petroleum. The mineralization, however, preceded the migration of petroleum into the uranium-bearing formation. The abundance of syngenetic uranium is in direct dependence on the abundance of primary organic matter. There was some redistribution of uranium during diagenesis resulting in the formation of flocculi, replacement of shells, and formation of concretions. In oolites the finely dispersed pitchblende forms the core and the separate concentric bands, making up to 30–50 percent of the oolite. Further redistribution occurred during the Alpine orogeny when pitchblende formed veinlets and stylolites. The geographical location of this uranium deposit and its economic importance are not indicated.

G. A. Pelymsky, *The influence of enclosing rocks on the process of ore deposition in hydrothermal uranium deposits* (pp. 39–51).

The author discusses the dependence of localization of uranium mineralization on the composition of wall rocks, especially in the skarn type deposits. The

uranium-bearing veins are generally associated with shear fractures and consist of quartz, carbonates, fluorspar, chlorite, hematite, pitchblende, and some sulfides. The ore shoots in veins are oriented parallel to the intersection of a vein with layers or lenses of favorable rocks, which are enriched in ferrous iron, calcium, magnesium, and sodium, and especially with those that contain much pyrite. The most favorable conditions for mineralization exist in pyritiferous biotite schists and paragneisses, skarns, and tuffites of basic rocks with skarn bands. Conditions favorable for uranium mineralization occur in kersantites, porphyrites, dolomitized limestones, diabases, and amphibole schists; quartzites quartz-muscovite schists, and granites are unfavorable. During the reaction of hydrothermal solutions with the favorable rocks, the alkalies and alkaline earths are removed. The physicochemical equilibrium of hydrothermal solutions changes due to the increase of pH. This results in precipitation of oxides and hydroxides. There is no change of the physicochemical equilibrium of solutions while they are passing through rocks which mostly do not react with the solutions. But colloform pitchblende is deposited as soon as the solutions are in contact with tuffites, skarns, and biotite schists. The quartz-carbonate-pitchblende mineralization is accompanied by silicification and red coloration due to the presence of iron oxide.

N. A. KHRUSHCHOV, *Classification of molybdenum deposits* (pp. 52–67).

The classification is genetic and the ore formations are arranged in the order of decreasing temperature of deposition. The group of endogenous deposits is represented by: (a) molybdenite ore formation in granites, syenites, aplites, and pegmatites (Dzhangryk in Kirghizia, Yankan in the Far East, Sokhatinka in Buryat ASSR, Ramona in California); (b) quartz-molybdenite formation in gneiss, granite, and crystalline schist, in places with W and Bi (Chikoy in Transbaikal region, Kharbey in the Urals); (c) molybdenite-scheelite formation in skarns, with W, Cu, sometimes Pb and Zn, accompanied by formation of skarns and hydrothermal alteration of skarns (Northeastern Caucasus, Northeastern China, Morocco); (d) quartz-wolframite with molybdenite formation in granites with hornfels in the hanging wall, with W, Sn, Bi and Be, and greisenization of wall rock (Central Kazakhstan, Transbaikal region, Southeastern China); (e) quartz-molybdenite-sericite formation in similar environment, in places with Au, Cu, and Re, sericitization and silicification of wall rock (Umal'ta in the Far East, Davenda in the Transbaikal region, Yugoslavia, Climax in USA); (f) quartz-molybdenite-chalcopyrite-sericite formation in granites and granodiorites, with Cu and Re, sericitization, silicification, and chloritization of wall rocks (Southwestern USA, Armenia, and Central Kazakhstan); (g) sulfide formation in metamorphic schist, with Cu, Au, Pb, and Zn, and rock alteration as above (Urup in Northern Caucasus, Aktyuz in Kirghizia); and (h) uraninite-molybdenite formation in granites and effusives, with uranium, carbonatization, chloritization, and kaolinization of wall rock (United States). The group of exogenous deposits is represented by the wulfenite formation in the oxidation zones of lead deposits in carbonate rocks, with Pb, Zn, and Au (Mammoth in USA, Kzyl-Espe in Kazakhstan), and by the carbonaceous-cherty and coal-bearing sediments containing U, V, and rare earths.

Ninety-five per cent of the world economic reserves of molybdenum are concentrated in deposits of the formations represented by associations of quartz-molybdenite-sericite, quartz-molybdenite-chalcopyrite-sericite, molybdenite-scheelite in skarns, and quartz-wolframite (scheelite) greisen with molybdenite. Large reserves of molybdenum are concentrated in the low-grade carbonaceous-cherty

and coal-bearing formation. Molybdenum deposits associated with the Alpine orogeny make 47% of the total reserves. The Mesozoic deposits make 23%, the Hercynian 21%, the Caledonian 3%, and the Cambrian 1% of the world reserves.

I. B. Borovsky, A. N. Deev, I. D. Marchukova, *Application of the method of local X-ray spectrum analysis to investigation of the platinum group minerals* (pp. 68–73).

The polished section is located in a special X-ray tube as a substitute for the anode. The microscopic structure of the section is examined through a metallographic microscope. A beam of electrons is focused on an area of the polished section in the order of one micron. The electron beam excites the characteristic X-ray radiation which forms a spectrum. The intensity fo each line of this spectrum is recorded by a photon counter. The amount of elements in the mineral examined is determined by measuring the intensity of lines corresponding to the radiation of the elements present in the sample by comparing them with the standards. The new method allows one to analyze samples containing any elements of two spectrometers and results of their practical application for quantitative analysis of platinum minerals in polished sections.

A. D. Genkin, *Conditions of occurrence and composition of platinum group minerals in ores of the Noril'sk deposit* (pp. 74–84, 8 plates).

A detailed mineragraphic study of copper-nickel sulfide ores of Noril'sk revealed the presence of platinum minerals that represent solid solutions and intermetallic compounds of Pt, Pd, Rh, Ir, Ru, Cu, Ni, Fe, Sn, Sb, Bi, Pb, Au, Ag, as well as sulfides, arsenides, possibly tellurides and selenides of the platinum group metals.

The ores of Noril'sk are associated with an intrusion of the differentiated gabbro-diabase emplaced in Permian formations. The ore is represented by the disseminated type in picritic and taxitic gabbro-diabases, disseminated mineralization in rocks underlying the intrusive, and by sulfide veins. The main ore minerals are pyrrhotite, chalcopyrite, and pentlandite. The platinum minerals occur in greatest amount in chalcopyrite veins and are the result of accumulation of platinum minerals in residual sulfide melt that was rich in copper. Commonly the platinum minerals occur in the upper selvage of veins within the magnetite rim. The platinum minerals were deposited later than the enclosing sulfides and form intergrowths with native gold and gold minerals. Unusual are intergrowths with galena and the association with graphite-magnetite veinlets. The presence of solid solutions of platinum with iridium (up to 8%), sperrylite, new lead palladium compound (Pd_4Pb), stibiopalladinite, and the new mineral-palladium sulfide was confirmed by means of X-ray spectrum analysis of polished sections.[1]

E. N. Sukhanova, *Coke formation in coal due to influence of a sulfide vein* (pp. 85–89).

Coke formed in the area of the copper-nickel deposit of Noril'sk when coal of Permian age was in contact with the diabase dikes. In one particular case the sulfide vein formed in the central part of the coal bed. The maximum thickness of the vein is 40 cm; 35 cm zones of coke formed on both sides of the vein. The coke contains 2.2% volatiles, while unaltered coal contains 16.5% volatiles. The

[1] See also review by M. Fleischer in *The American Mineralogist*, March–April, 1961, p. 464.

sulfides fill fractures in the coke. The predominant ore mineral is pyrrhotite. It is accompanied by pentlandite, with some chalcopyrite, pyrite, and magnetite. The amount of chalcopyrite increases outside the contact of the vein with the coke. The content of platinum increases with an increase in the amount of copper. Microscopic study indicates that there was pseudomorphic replacement of the humic component of coal by pyrrhotite and chalcopyrite. The coke formed as the result of contact with sulfide melt which probably had a temperature of 600° C.

YU. I. NAZAROV, *Features of the deposition of barite and sulfides of nonferrous metals in Madneuli deposits* (pp. 90–101).

The deposits of Madneuli are located in Georgia. The country rocks are of Upper Cretaceous age and consist of volcanic tuffs, albitophyres, and lava breccia. The formation of the deposits was associated with tear fractures. The reaction of hydrothermal solutions with the country rocks resulted in a metasomatic character of mineralization. The ore deposits belong to two types of mineralization—the barite-sphalerite and the chalcopyrite-pyrite. There is a suggestion of a genetic relationship between the ore deposits and the subvolcanic sources which produced the Tertiary dacite extrusives. The presence of secondary quartzites[1] with limonite coloration when weathered, baritized rocks, gypsum veins in volcanic rocks and fractured and brecciated rocks are favorable guides in prospecting for similar ore bodies.

T. V. IVANITSKY, *The hydrothermal metamorphism of the country rocks in lead-zinc and base metals deposits of Georgia* (pp. 102–113).

The hydrothermal deposits of southern Georgia occur in different sedimentary, volcanic, and intrusive rock formations. Those of greatest interest are the volcanic series of Bajocian, Upper Cretaceous, and Eocene age. Hydrothermal rock alteration resulted in the formation of secondary quartzites, which are characteristic in the Upper Cretaceous volcanic acid series. The wall-rock alteration in the areas of propylitized rocks is represented by carbonatization and kaolinization of rocks. Dolomitization developed in carbonate rocks around the low temperature lead-zinc deposits. Detailed mapping of areas of hydrothermal metamorphism is a prerequisite in prospecting for ore deposits.

Brief Communications

G. M. KONSTANTINOV, *A new type of tin ore in dolomites of the Malyi Khingan* (pp. 114–116). An unusual type of mineralization was discovered in dolomites of the Malyi Khingan Mountains by means of geochemical prospecting. The mineralization is represented by metasomatic elongated ore bodies of irregular shape in Upper Proterozoic dolomite series intruded by the Variscan granodiorites and dikes of andesite and plagioporphyry. There are two distinct zones characterized by the cassiterite-pyrite mineralization with siderite and by the cassiterite-arsenopyrite-boulangerite mineralization.

S. YA. LIOGEN'KY, *Physical properties of pegmatites and enclosing rocks of Karelia and Kola Peninsula* (pp. 117–120). The author summarizes data on density, magnetic susceptibility, residual magnetization, and specific electric

[1] Rocks of hydrothermal-metasomatic origin which consist of quartz, sericite, alunite, pyrophillite, kaolinite (dickite), andalusite, and diaspore.

resistivity of gneisses, amphibolite, gabbronorite, and pegmatites with the purpose of selecting properties which may be used in prospecting for high-grade mica deposits in pegmatites. The electric resistivity method was found to be the best to outline the boundaries of pegmatitic bodies.

Discussion and Bibliography

V. L. Barsukov and G. B. Naumov discuss the article by A. G. Betekhtin on the behavior of radioactive elements during the process of formation of endogenous deposits [1] (pp. 121–124). The topics discussed deal with the form in which uranium is transported by the hydrothermal solutions, the role of free oxygen in precipitation of UO_2, and the role of the country rock in the localization of uranium mineralization. This discussion is followed by A. G. Betekhtin's reply (pp. 124–127).

A. D. Shcheglov, considering the problem of genesis of tungsten deposits of the Transbaikal region (pp. 127–130), discusses the papers by V. F. Barabanov, published in 1952 and 1959, emphasizing the role of internal pressure during the process of mineralization, paragenesis of minerals in tungsten-bearing veins, and formation of some minerals in ore bodies from material introduced from the country rock into the veins.

EUGENE A. ALEXANDROV

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COLUMBIA UNIVERSITY,
June 12, 1961

Geosynklinale Lagerstetten, was dazu gehört und was nicht dazu gehört, sowie deren Beziehungen zu Geotektonik und Magmatismus. (Geosynclinal ore deposits, what and what not belongs to them, as well as their relationship to geotectonics and magmatism.) By HERMANN BORCHERT. Pp. 61; figs. 7, Freiberger Forschungshefte, Heft C 79, April 1960.

The subject of this article is one of the largest and most complex geologic and genetic problems. The author used a number of fairly recent publications, including several of his own, in an attempt on a draft-synthesis. He emphasized the growing number of ore deposits, which are to be considered to be of geosynclinal magmatic origin. A short time ago the German Lahn Dill-iron formation was accepted as the sole representative of this group. Since then other initial magmatic deposits, containing copper and zinc (Leksdal, Ergani, Meggen) and numerous meso and epithermal ore deposits (among them Rammelsberg, Borovica, Mount Isa) are declared to be derived from geosynclinal magmatism. The materials of these volcanic ore deposits are considered as products of the rest-liquids of the early geosynclinal intrusions. Classical deposits of early crystallization (chromite, titanomagnetite, magnetite-apatite, a.s.o.) are similarly listed under the heading of early geosynclinal period. The author asserted, that the minette- and Lake Superior-type iron ores are not "geosynclinal" and their iron-content came not from the eroding continents, but from marine water. The synorogene and late-orogene phases are marked by the well known pluton-subvolcan series of molybdenite, wolframite—antimonite, cinnabar minerals. Borchert is against reducing the concept of geosynclinal ore deposits to products of the early geosynclinal and initial magmatic activity. He proposed not to

[1] Reviewed in ECONOMIC GEOLOGY, vol. 56, no. 1, January–February, 1961, pp. 219–220.

make the division between geosynclinal and non-geosynclinal, but rather between juvenile-basaltic and sialitic-palingenetic deposits.

This article touches on a great amount of partly or completely unsolved questions, on obvious contradictions and proves to be an indicator of our present stand of knowledge on basic geological issues. A list of 273 publications, mostly written during the past decade, follows the paper.

ERVIN G. OTVOS

Geology of the U.S.S.R.—A Short Outline. By D. V. NALIVKIN, translated by S. I. TOMKEIEFF. Pp. 170; map. Pergamon Press, New York, 1961. Price, $15.00.

This little book is Volume 8 of the International Series of Monographs of Earth Sciences. It also includes a colored geological map in two sections of the U.S.S.R. on a scale of 1:7,500,000. It is the first compact and comprehensive account of the geology of the U.S.S.R. ever published in Russian. This book covers a territory that is about one-sixth of the total land surface of the earth.

The ten chapters are arranged on the basis of geologic-geographic provinces. They are: Russian Platform, Siberian Platform, West Siberian Lowlands, Ural Mts., Western Arctic and Timan, Angara Geosyncline, Central Asia, Mediterranean Geosyncline, N. border of the Mediterranean Geosyncline, N.W. border of the Mediterranean Geosyncline, and Pacific Ocean Geosyncline. Under each of these the content is divided into five divisions, Relief, Stratigraphy, Tectonics, Magmatism, and Economic Deposits. There is appended a Table of Geologic Formations in the U.S.S.R. and a list of orogenic and magmatogenic epochs. About 3 to 5 pages of each chapter are devoted to mineral deposits, mostly a sentence regarding each economic product.

The book gives an excellent bird's-eye-view of the geology of each of the provinces. The geologic map prepared for this edition is a fine example of geologic cartography.

The Precambrian Geology and Geochronology of Minnesota. By SAMUEL S. GOLDICH *et al.* Pp. 193; figs. 37; pl. 5. Univ. of Minnesota Press, Minneapolis, 1961. Price, $4.00.

This is a cooperative effort of many individuals and scientific organizations. It starts with a discussion of the problems, which is followed by 28 pages of discussion of the different methods and procedure and evaluation of geochronology.

The main part of the book is devoted to detailed discussions of the geology and geomomonology of the three chief geologic-geographic provinces and the various regions within them: The stratigraphy and igneous rocks of early middle and late Precambrian time and their geologic history are described in detail, followed by discussions of the ages. A last chapter takes up the "Development of a Precambrian Classification" in which the principles and the problems are outlined and chronology recommended for each of the Precambrian divisions. A comparison is given of the age dating in Minnesota and Finland.

The book is a handy reference on the Precambrian of Minnesota, and also of north central United States.

BOOKS RECEIVED

ROGER L. AMES AND ERIC S. CHENEY

An Introduction to the Methods of Optical Crystallography. F. DONALD BLOSS. Pp. 294. Holt, Rinehart and Winston, Inc., New York, 1961. Price, $7.00. *Methods of identifying crystals by the polarizing microscope utilizing the optical indicatrix, for beginners. Covers microscopes, light, isotropic, uniaxial and biaxial crystals; 3 appendices on properties of ellipses, optical tables and recording data.*

Beerman's All Mining Year Book, 1961. Pp. 479. R. Beerman Publishers, Capetown, 1961. Price, £3 3s. *A handy reference to mines of southern Africa, grouped under metal and mineral produced, giving properties, uses, statistics, corporate set-up and all producing mines. A good reference book, well done.*

Field Geology, 6th Edit. FREDERICK H. LAHEE. Pp. 925; figs. 641. McGraw-Hill Book Co., New York, 1961. Price, $10.75. *For 45 years this book has ranged through six editions; it retains its former features but is brought up to date, with inclusion of many new topics and new references. It will still remain the standard text and reference on field geology.*

Geology of India and Burma, 4th Edit. M. S. KRISHNAN. Pp. 604; pls. 22; figs. 14; tables 80, maps 17. Higginbothams (Private) Ltd., Madras-2, 1960. Price, Rs. 22.50. *This book is both a text for post-graduate students and an advanced treatise on Indian stratigraphy. Introductory material has been added to the systems of the Phanerozoic Eon for comparison with western Europe and to delineate the faunal and floral affinities of the southern continents which composed Gondwanaland.*

Boletin Geominero Santiagueño #1. Provincia Manganifera Santiagueño-Cordobesa. ALEJANDRO GAMKOSIAN, R. M. UMLANDT and A. C. JANSSON. Pp. 40; figs. 9; tbls. 7; maps 2—scale 1/100,000. Sgo. del Estero, Republica Argentina, 1960. *Twenty-five manganese districts within 2,000 sq km constitute a manganiferous metallogenic province. The psilomelane-pyrolustie ore is in veins up to 1,000 meters in length, varies between 20% to 40%, and is believed to be of colloidal origin.*

The Australian Mineral Industry—Quarterly Review and Quarterly Statistics, Vol. 13, No. 3, March, 1961. Pp. 22. Price, 6/–. Bureau of Mineral Resources, Geology and Geophysics, Canberra. **Os Grandes Diamantes Brasileiros.** ESMERALDINO REIS. Pp. 66; pls. 23; map. Bol. 191, Departamento Nacional da Produção Mineral, Rio de Janeiro, 1959. *A general review of the scattered data on Brazilian diamonds.*

Administration Report of the Government Mineralogist for 1959. L. J. D. FERNANDO. Pp. 37. Price, –/95. Ceylon Department of Education, Science and Art, 1960. In Indian and English. *The most important work carried out was a survey of limestone formations in connection with a proposed cement factory.*

Overseas Geology and Mineral Resources, Vol. 8, No. 2. Pp. 251; figs. 5; pls. 4. Price, 10s. Overseas Geological Surveys, London, 1961. *Contains three articles, two on geology, and a series of annual reports from the overseas surveys.*

Geology of the Country Around Monmouth and Chepstow. F. B. A. WELCH and F. M. TROTTER. Pp. 155; pls. 2; figs. 11. Memoirs of the Geological Survey of Great Britain, London, 1961. *The Upper Old Red Sandstone unconformably*

overlies the Lower Old Red Sandstone and the Silurian Ludlow Series north of the Severn River.

Bauxite in Bihar, Madhya Pradesh, Vindhya Pradesh, Madhya Bharat and Bhopal. M. K. Roy Chowdhury. Pp. 271; figs. 3; maps 5—scales ¼″/1 mile, 1″/32 mi., and 1″/20 mi. Price, Rs. 18. 18.50 or 28sh. 6 d. Memoirs of the Geological Survey of India, Vol. 85, Delhi, 1958. *Increased interest in bauxite stimulated this report. A reconnaissance survey has discovered several new ore-bodies, but the lack of drilling prevents detailed statements on the quality and extent of ore. Total reserves in the four states are estimated at a minimum of 21 million tons.*

Geological Survey of Japan, Tokyo, 1961. Geological maps, scale 1/200,000. Aomori, Tokushima, Yokohama (oil and gas, 1/50,000). Stories of Resourcefull Kansas Featuring the Kansas Landscape. Grace Muilenburg, Editor. Pp. 44. Pamphlet 1, State Geological Survey, Lawrence, 1961. *Brief descriptions of geological features of Kansas written for the layman.*

Geology maps and text of NE Flint Creek Range and Drummond area, Nos. 4 and 5. Montana Bureau of Mines and Geology, Helena, 1961.

Vol. LXIX, Pt. 1, 1960. Ontario Department of Mines, Toronto, 1961. Pp. 48. *Four reports: statistical review of the mineral industry for 1959, mining accidents in 1959, and classes for prospectors, 1959–60.*

Bulletin of the Geological Survey of Taiwan, No. 12. Taipei, China, 1960. *The articles in this issue include a biographic study of the Miocene of western Taiwan, the stratigraphy of the Tananao schist in northern Taiwan, and the geology of the Nantao and Alishan coal fields. An English translation of each article appears in the last half of the volume.*

Die Geologie van die Gebied Om Volksrust. H. N. Visser, J. F. Cillié and F. J. J. Fürter. Pp. 134; pls. 15. Price, £1. 11s. Geological Survey of the Union of South Africa Pretoria, 1960. *Five coal beds and an oil shale have economic potential in this area. English summary.*

Petrology of the Mount Airy "Granite." R. V. Dietrich. Pp. 63; pls. 18; figs. 6; tbl. 1. Bulletin of the Virginia Polytechnic Institute Engineering Experiment Station Series No. 144, Vol. LIV, No. 6, Blacksburg, April, 1961. *The rock, actually a leucogranodiorite, studied in a quarry, appears to be of igneous origin with late- or post-kinematic intrusion and consolidation of the magma under high pressure.*

Western Australia Government Cehmical Laboratories Report for the Year 1959. Pp. 21; tbls. 14. *Annual report from agriculture, food and drugs, fuel technology, industrial chemistry, and geochemistry divisions.*

Geological Survey, British Territories In Borneo—Kuching, 1959–1960.

Geological Report 1959. F. W. Roe. Pp. 219; pls. 46; figs. 26; tbls. 26. *Mineral resources accounted for 70% of all exports. Bauxite, oil and gold production increased. Coal, chromite, copper, limestone, asbestos and stone and gravel have been discovered and detailed prospecting initiated by private companies. 90% of the Territories has been mapped or is currently being surveyed.*

Memoir 11. The Geology and Mineral Resources of the Lower Rajang Valley and Adjoining Areas, Sarawak. E. B. Wolfenden. Pp. 167; pls. 39; figs. 15; tbls. 26. Map, scale 1/250,000. Price, M$6.00 or 14 shillings. *The area is almost entirely underlain by Upper Cretaceous to Recent sediments; a few Tertiary igneous rocks also occur. The geosynclinal Cretaceous to Eocene*

rocks have been intensely folded and mildly metamorphosed. Quaternary deposits build extensive coastal plains and the large Rajang Delta. Mineral and petroleum resources are few; however, search for the latter continues.

Bull. 3. The Geology of Sarawak, Brunei and the Western Part of North Borneo. P. LIECHTI, F. W. ROE, N. S. HAILE and H. J. C. KIRK. Pp. 360; pls. 73; figs. 30. Map, scale 1/500,000. Price (both vols.) M$21 or £2—9. *This is the first comprehensive report, compiled largely by the Royal Dutch Shell Group, of the geology to be published. The formations range from pre-Permian to Recent, but 32 Upper Cretaceous to Recent geosynclinal formations underlie 98% of the area. Three pre-Tertiary folding phases and four local Tertiary ones have been distinguished. Volume II consists of a geologic map, columnar sections, and a tectonic map.*

University of California Publications in Geological Sciences—Berkeley and Los Angeles, 1961.

Vol. 34, No. 7. Paleoecologic Molluscan Geography of the Californian Pleistocene. J. W. VALENTINE. Pp. 309–442; figs. 16. Price, $2.50. *Nine district Pleistocene molluscan populations are recognized and related to Pleistocene glaciation.*

Vol. 37, No. 3. Foraminifera from the Sacate Formation South of Refugio Pass, Santa Barbara County, California. G. R. HORNADAY. Pp. 165–232; pls. 13; figs. 6. Price, $2.00. *Eighty late Eocene foraminifer species are recorded permitting the Sacate formation to be correlated with other formations on the Pacific coast.*

Vol. 40, No. 1. Californian Pleistocene Paleotemperatures. J. W. VALENTINE and R. F. MEADE. Pp. 46; figs. 4. Price, $1.00. *Paleotemperatures determined by paleoecology and oxygen isotope ratios are compared and found to be in close agreement.*

California Department of Natural Resources—San Francisco, 1960–1961.

Supplement to Minerals of California for 1955 through 1957. JOSEPH MURDOCH and R. W. WEBB. Pp. 64. Price, $1.00. *This paper reports additional minerals, listed by county, and with an individual authority cited for each occurrence.*

Geologic Map of California. Kingman Sheet, scale 1/250,000. Price, $1.50.

Spec. Rept. 65. Geology of the San Bernardino Mountains North of Big Bear Lake, California. J. F. RICHMOND and C. H. GRAY, JR. Pp. 68; figs. 72; tbl. 1; map 1—scale 1/24,000. Price, $1.50. *The area is underlain by Paleozoic sediments, Mesozoic igneous rocks, and Cenozoic clastic sedimentary rocks. Placer gold has been successfully mined in the area, but other metals are present in sub-ore grade.*

Geological Survey of Canada—Ottawa, 1960–1961.

Bull. 63. Cretaceous Rocks in the Region of Liard and MacKenzie Rivers, Northwest Territories. D. F. STOTT. Pp. 32; plates 4; figs. 4; tbl. 1. Maps 2 —scales 1″/30 miles and 1″/8 miles. Price, 75 cents. *A stratigraphic report on the marine Lower Cretaceous, marine and non-marine Upper Cretaceous rocks, with possible relation to petroliferous rocks to the south.*

Bull. 64. Gneisses of the Kipawa District, Western Quebec, Grenville Sub-Province of Canadian Shield. W. T. HARRY. Pp. 25; figs. 10. Price, 50

cents. *The banded gneiss complex has been intruded by a granodioritic and younger granitic gneiss; the area has undergone a paracrystalline deformation.*

Bull. 69. Design of a Curie Point Meter. A. LAROCHELLE. Pp. 14; plate 1; figs. 7, tbl. 1. Price, 50 cents. *The instrument described is a torsion-balance type, using a photoelectric recording mechanism. Details of the various components of the instrument and an outline of its calibration are discussed.*

Bull. 74. The Jurassic Faunas of the Canadian Arctic. Middle and Upper Jurassic Ammonites. HANS FREBOLD. Pp. 43; pls. 21; figs. 3; tbls. 1. Price, $2.00. *This detailed study of ammonite faunas permits correlation of the associated Jurassic rocks and shows their faunal and stratigraphic relationships with East Greenland and Siberia.*

Paper 60-22. Ground-Water Resources of Plum Coulee Area, Manitoba. J. E. CHARRON. Pp. 81; pls. 2; figs. 9; tbls. 5. Price, 50 cents. *The chances of finding good potable water by digging or drilling a well in the area do not appear good.*

Paper 60-23. Preliminary Report on Hydrogeology, Ottawa-Hull Area, Ontario and Quebec. L. V. BRANDON. Pp. 17; pl. 1; figs. 4; tbls. 3. Map 1, scale 1/63,360. Price, 50 cents. *The sand layers within glacial deposits store and transmit a much greater quantity of water than all the rock formations. No evidence exists of a significant change in ground-water levels in the past decade.*

Paper 60-24. Tectonic Framework of Southern Yukon and Northwestern British Columbia. H. GABRIELSE and J. O. WHEELER. Pp. 31; figs. 6. Map 1, scale 1″/20 miles. Price, 50 cents. *A synthesis of available information and interpretation of the tectonic features.*

Paper 60-31. Belleville and Wellington Map-Areas, Ontario. B. A. LIBERTY. Pp. 9; maps 2—scale 1″/1 mile. Price, 50 cents. *Text contains stratigraphic descriptions for the accompanying maps.*

Paper 60-32. Buried Valleys in Central and Southern Alberta. A. MAC S. STALKER. Pp. 13; pl. 1. Map, scale 1/267,200. Price, 50 cents. *Pleistocene glaciers strongly modified and disrupted preglacial drainage, and caused modern rivers to flow long distances through entirely new channels.*

Paper 60-33. A Preliminary Study of Canadian Metallogenic Provinces. A. H. LANG. Pp. 54. Maps 3, scale 1/7,603,200. Price, 50 cents. *At the request of the International Geological Congress an attempt has been made to delineate the metallogenic (Be, Cu, Cr, Au, Fe and Ti, Pb and Zn, Li, Mn, Hg, Mo, Ni and Co, Nb, Sn, W, U and V) of Canada. Each geologic province of the country and its ores are described briefly.*

Paper 61-6. The Sequence of Marine Triassic Faunas in Western Canada. E. T. TOZER. Pp. 17; fig. 1; tbl. 1. Price, 25 cents. *A taxonomic description of three benthonic faunas.*

Geologic maps, scale 1/253,440. No. 3-1961, **Quesnel, B. C.**; 14-1961, **Nahanni, B. C.**; 44-1960, **Shelburne, N. S. Aeromagnetic maps,** scale 1/63,360, 887–889g, **Laughton, McCoy, Petownikip Lakes, Ont.**

Geologic Maps, scale 1/253,440. Map 43-1960, **Mingo Lake, Baffin Land**; 41-1960, **Big Bald Mt., N. S.**; 50-1960, **North Spirit Lake, Ont.**; 48-1960, **St. Mary Bay, N.S.**; 52-1960, **Whiskey Jack Lake, Man.**; 1-1961, **Hopewell, N. S. Geologic map (colored),** scale 1/63,360, **Perth, Ontario. Drift-thickness contours,** scale 1/18,000, **Montreal Area, Quebec.**

Aeromagnetic Maps, scale 1/63,360. Maps 1029g–1044g. **Egenolf, Whitmore, Colbeck, Erickson, Snyder, Thanout, Hugill, Finner, Turner, Sucker, Kasmere, Wolk, Veal, Tice, Putahow, and Bagg Lakes, Manitoba**; Geology, scale 1/253,440, Map 8-1961, **Miminiski and Caribou Lakes, Ontario.**

Geologic maps, scale 1/63,360; **Dean and Wakwekobi Lakes, Ont.** 5 and 6-1961; **Sevogle, N. B.; Rabbit River, B. C.** (scale 1/253,440).

Index sheets (scale 1/1,000,000), **British Columbia and Alberta.** Nos. 82, 83, 93, 94, 103, 104, 114E.

Geology maps, scale 1/253,440. **Tay River and Sheldon Lake, Yukon,** Nos. 12, 13; **Montreal area geology,** 1/18,000, No. 29; Paper 61-8, **Triassic of Rocky Mts. and Foothills.**

Illinois Geological Survey—Urbana, 1961.

Circ. 318. Underground Storage of Natural Gas in Illinois. A. H. BELL. Pp. 27; figs. 17; tbls. 9. *Natural gas from the Mid-Continent and Gulf Coast is being stored in two main types of reservoirs: 1) aquifers that originally contained only water, and 2) those that contained oil or gas as well as water.*

Oil and Gas Industry in Illinois. W. F. MEENTS and A. H. BELL. Map, scale 1 inch/8 miles. *The map shows oilfields, pipelines, refineries, and underground storage facilities.*

Idaho Bureau of Mines and Geology—Moscow, 1961.

Bull. 16. Guidebook to the Geology of the Coeur D'Alene Mining District. R. R. REID, Editor. Pp. 37; figs. 19, tbl. 1. Price, $1.25. *This guidebook was prepared for the 1961 meetings of the Association of American State Geologists. District history and general geology are treated before the detailed geology of five representative mines.*

Bull. 17. Economic Geology of Central Idaho Blacksand Placers. C. N. SAVAGE. Pp. 160; figs. 35 (including maps); tbls. 30. Price, $2.50. *Most of Idaho's blacksand deposits have been worked for gold, monazite, garnet, and niobium-tantalunm minerals, but yttrium, zirconium, hafnium, uranium and thorium are also potentially valuable.*

Bull. 18. Idaho's Mining Industry . . . the First Hundred Years. Pp. 71. Price, $1.50. *This book is written on the secondary school level to acquaint Idahoans with past, present, and future aspects of mining in the state as it prepares to commemorate the centennial year of its creation as a Territory.*

Indiana Geological Survey—Bloomington, 1961.

Rept. of Progress 24. Refractory Clays of Indiana. J. L. HARRISON. Pp. 18; fig. 1; tbls. 7. Price, 25 cents. *Large reserves of clay suitable for low-duty refractory products are present in southwestern Indiana.*

Field Conference Guidebook 10. Stratigraphy of the Silurian Rocks of Northern Indiana. R. H. SHAVER AND OTHERS. Pp. 62; figs. 6; tbl. 1. Price, $1.00. *The field conference treats the basic stratigraphy of the Silurian rocks that lie between the Cincinnatian rocks and the bedrock series in the northern half of Indiana.*

Northern Rhodesia Geological Survey—Lusaka, 1960–1961.

Rept. 9. The Geology of the Sinda Area—Explanation of Degree Sheet 1431, NE. Quarter. K. A. PHILLIPS. Pp. 27; pls. 2; tbls. 3. Map Scale

1/100,000. Price, 15s. *This report, admittedly descriptive rather than conclusive, describes one portion of a pluton and the country rocks (granitized gneisses) which are similar to the Basement Complex described elsewhere in Northern Rhodesia.*

Annual Report of the Department of Water Affairs for the Year 1960. Pp. 8. Price, 2s.

Pennsylvania Geological Survey—Harrisburg, 1961.

Bull. G35. Guide to the Geology of Cornwall, Pennsylvania. CARLYLE GRAY and D. M. LAPHAM. Pp. 18; pls. 2; figs. 5. *The history of mining operations from 1742 to the present is briefly reviewed. The ore is spacially and genetically related to a Triassic dike, although somewhat later in time than the crystallization of the diabase.*

Bull. M40. Well-Sample Descriptions in Northwestern Pennsylvania and Adjacent States. C. R. FETTKE. Pp. 691, pls. 4. *A description of rock cuttings from 52 wells drilled in the search for oil and gas.*

Bull. M43. Uranium in Pennsylvania. J. F. MCCAULEY. Pp. 71; pls. 9; figs. 13; tbls. 11. *The great majority of the 43 uneconomic uranium occurrences are in the Devonian Catskill formation. No primary uranium minerals were found in these sandstones. Sulfur isotopic data is cited as supporting a ground water hydrothermal theory of origin.*

Spec. Bull. 9. Oil and Gas Field Atlas of the Foxburg Quadrangle, Pennsylvania. J. M. BERGSTROM and LILLIAN A. HEEREN. Pp. 26; pls. 4; maps 9, scale 1/2,000.

Serviços Geológicos de Portugal—Lisboa, 1959–1960.

Vol. XIV—Fascs. 3–4. Estudos, Notas e Trabalhos do Serviço de Fomento Mineiro. Pp. 200. *These numbers include articles on magnetic prospecting, crystalline limestones, x-ray study of a zoned phosphate-rich pegmatite, x-ray analyses of particles in the lungs of miners who have died of pneumonia, an ancient Roman mine and living quarters, and a summary of the 1958 activities of the Serviço de Fomento Mineiro.*

Technical Paper 26. The Ore Controls of Some Uranium Vein Deposits in Portugal. J. CAMERON. Pp. 62; figs. 9; tbls. 11. *Uranium is presumed to have been leached from the Hercyman granites during a later period of deformation.*

Memória 3—(Nova Série). Étude Structurale de L'Aire Typhonique de Caldas da Rainha. GEORGES ZBYSZEWSKI. Pp. 184; pls. 11; figs. 5. *A detailed report on the stratigraphy, structure, and economic geology of the Caldas area north of Lisbon. Emphasis is given to the salt tectonics associated with the Mesozoic rocks. In French.*

Quebec Department of Natural Resources—Quebec, 1961.

Outline of Progress of the Mining Industry in the Province of Quebec during the Year 1960. Pp. 29; pls. 4; tbl. 1. *The value of the mineral production in the Province was over $441 million. Nine of the 13 metallics registered gains. The progress of individual companies in each district is reviewed.*

List of the Principal Operators and Owners of Mines and Quarries in the Province of Quebec. Pp. 81. *Addresses are listed for the principal producers of about 45 substances.*

South Dakota Geological Survey—Vermillion, 1961.

Misc. Investigations 2. Possible Underground Storage of Natural Gas in South Dakota. A. F. AGNEW. Pp. 10; figs. 3; tbl. 1. *Several possible areas of underground gas storage are suggested near the Black Hills and in Harding and Butte counties.*

Rept. of Investigations 89. The Resistivity Method Applied to Ground Water Studies of Glacial Outwash Deposits in Eastern South Dakota. DANIEL LUM. Pp. 24; figs. 32. *The horizontal traverse method is more useful than the depth profile method in locating favorable sites for water test wells by detecting and outlining stream deposits in till.*

Geological Survey of Sweden—Stockholm, 1960.

No. 16. Description to Accompany the Map of the Pre-Quaternary Rocks of Sweden. N. H. MAGNUSSON, P. THORSLUND, F. BROTZEN, B. ASKLUND and O. KULLING. Pp. 177; figs. 68. *The cycles of the Swedish Precambrian, from youngest to oldest, are pre-Gothian, Svionian, Karelian, Gothian and Dalslandian. The Cambro-Silurian, Mesozoic, and Tertiary histories are also reviewed and the geology of the Caledonian Mountain Chain and the Caledonides of Swedish Lapland are discussed.*

Iron and Sulphide Ores of Central Sweden. N. H. MAGNUSSON. Pp. 48; figs. 30. *This guidebook for the International Geologic Congress XXI describes the iron, manganese, and sulfide ores and their host rocks which are restricted to the volcanics of the Svecofennian cycle.*

Economic Geology
Vol. 56, 1961, pp. 1170–1177

SOCIETY OF ECONOMIC GEOLOGISTS INCORPORATED

PROCEEDINGS FOR SOCIETY YEAR 1960

Report of the President

Society Year 1960 has been an active one. The two regular meetings of the Society, at Denver and at St. Louis, were well attended, and the papers read were of a high calibre. An additional gathering of an internationally representative group of the membership was made possible when the International Geological Congress was held in August of 1960 in Copenhagen. While a technical session was not feasible, due to the heavy schedule of the Congress itself, a dinner meeting was held, which was well attended and happily included representatives of our membership from many parts of the world.

The meetings in Copenhagen pointed up a growing interest in, and the importance of, the international function of the Society, and a number of members from countries outside North America voiced the hope that this aspect of its work should receive more attention. The vastly increased amount of geological work in the economic field now being done by internationally-financed organizations and by governmental agencies in itself serves to emphasize the increasing opportunity and need for expanded effort on the part of an international organization devoted to the advancement of the science of economic geology.

With these thoughts in mind, I proposed to the Council that, in addition to the Regional Vice-Presidents, a National Representative should be appointed for each country where the Society has any appreciable number of members. The Council approved this proposal and representatives were appointed forthwith. (See the Secretary's Report.) It is hoped that this move not only will enable the Society to keep more closely in touch with its far flung membership, but eventually that it may make it possible, in collaboration with local societies, to organize regional meetings of the Society in countries outside North America.

Closely allied with the problem of expanding the international interests of the Society is the problem of maintaining a high calibre and fully representative membership. In this connection, the Committee on Perpetuation of the Society, under the able Chairmanship of Hugh E. McKinstry, has been most effective. Much of the renewed interest in the work of the Society on the part of outstanding men in the profession, both at home and abroad, is due, in large degree, to the activities of this Committee. In this connection, it is particularly gratifying to note that a relatively large percentage of the 92 new members elected during the past year are well known, widely experienced men, who for some reason had not joined the Society earlier; that a fair number are expert in the experimental aspects of mineralogy, geology, geochemistry, and geophysics; and that roughly 27% of the total number elected are from countries outside North America.

I would also like to acknowledge our indebtedness to the Council and the various Committee members, all of whom gave unstintingly of their time and talents to further the interests of the Society. In particular, I would pay tribute to the able and energetic work of the Secretary and of the Treasurer. I think every member of the Society should know that without the selfless and conscientious efforts of these officers, the work of the Society would founder.

Harold M. Bannerman, who has held the position of Secretary since 1957 asked to be relieved of this duty at the end of the Society Year. His guidance and energy during his Secretaryship has earned the respect and gratitude of the whole membership, and, over the past year that I have been President, I have been particularly glad of his wise counsel. The position of Secretary has been assumed by Eugene N. Cameron, Professor of Economic Geology at the University of Wisconsin, whose experience, interests, and close association with Society affairs, makes him well fitted to carry on the high tradition of service set by previous Secretaries.

All in all, I think the record will show that 1960 was a good year in the annals of the Society and that its affairs are in a healthy state. Its opportunity for service to the profession is on the increase throughout the Free World; so too is the interest in its work. I am most appreciative of the high privilege accorded me to serve as its President.

DUNCAN R. DERRY, *President*

Report of the Secretary

Meetings of the Society.—Two technical meetings of the Society were held during Society Year 1960: one with the Geological Society of America and Associated Societies at Denver, Colorado, October 31–November 2, 1960; the other with the AIME at St. Louis, Missouri, February 27–March 2, 1961. The program and abstracts of papers presented before the Denver meeting were printed in Economic Geology, Volume 55, Number 6, September–October 1960, pp. 1323–42. The program and abstracts of papers presented at the St. Louis meeting were printed in ECONOMIC GEOLOGY, Volume 56, Number 1, January–February 1961, pp. 236–38.

The Presidential Address "Economic Aspects of Archean-Proterozoic Boundaries" was delivered by President Derry at Denver on Monday, October 31, and is printed in ECONOMIC GEOLOGY, Volume 56, Number 4, June–July 1961, pp. 635–47. Following the Presidential Address, the Annual Luncheon was held in the Spring Court Room of the Denver-Hilton Hotel.

The Society also held a dinner meeting at Copenhagen, Denmark, on August 18, during the meetings of the International Geological Congress. This meeting, which was presided over by President Derry, was attended by 275 members and their guests, and was addressed by Professor Kingsley Charles Dunham, Regional Vice President for Europe, who spoke on "New Developments in Geology."

Meetings of the Council.—The Council met at Denver on October 30–31 and again at St. Louis on March 1–2.

Committees.—The following Committees were approved for Society Year 1961:

Program Committee
Harold L. James, Chairman
W. M. Fiedler
W. F. Jenks
Charles F. Michener
W. P. Hewitt
H. V. Warren
H. V. W. Donohoo

Program Policy Committee
Charles F. Park, Jr., Chairman
Weston Bourret
John K. Gustafson
Robert S. Moehlman
Harold M. Bannerman
Herbert E. Hawkes, Jr.

Admissions Committee
John C. Frye, Chairman
Vincent C. Kelley
Ward C. Smith
Ralph Tuck
Frank Zurbrigg

Finance Committee
Vincent D. Perry, Chairman
Olaf N. Rove
Joseph T. Singewald, Jr.

Nominating Committee
S. Warren Hobbs, Chairman
G. Donald Emigh
Donald M. Fraser

Publications Committee
P. J. Shenon
Charles F. Park, Jr.
H. R. Gault

Auditing Committee
A. Nelson Sayre, Chairman
Thor H. Kiilsgaard

Research Committee
R. M. Garrels, Chairman

Richard M. Garrels Vincent E. McKelvey James M. Harrison	Term expires 1962
Robert M. Foose Herbert E. Hawkes, Jr. Stanley E. Jerome	Term expires 1963
Richard H. Jahns Charles Meyer Edwin W. Roedder	Term expires 1964

Committee on Perpetuation of the Society
Duncan R. Derry, Chairman
Joseph L. Gillson
Frederic M. Chace
William D. Johnston, Jr.
Eugene N. Cameron

Representative to AAAS
E. F. Osborn
Konrad B. Krauskopf

Representative to National Research Council
Walter S. White

On recommendation of the Program Policy Committee, Council approved plans for a symposium on "Chemical Weathering with Emphasis on Laterization" to be held at Cincinnati, Ohio, on Wednesday, November 1, 1961 (the day prior to the opening of the general sessions of the GSA and Associated Societies). The plan calls for two technical sessions—one composed of papers dealing primarily with theoretical considerations and experimental data; the other with papers dealing mainly with case studies.

Waldemar Lindgren Citation Awards for Excellence in Research.—On advice of an *ad hoc* committee on ground rules (Robert M. Garrels, Vincent E. McKelvey, and Patrick M. Hurley), Council approved the following rules to govern the selection of recipients of the Waldemar Lindgren Awards for Excellence in Research:

1. The Awards will be conferred upon "geologist whose research as college and university students result in papers of high merit on a subject judged important to economic geology."
2. Each Award shall consist of an appropriately inscribed citation and $100 in cash.
3. Any student who is, or who has been within the calendar year in which the paper is submitted, a candidate for a degree in any recognized college or university is eligible to enter the competition.
4. The selection of the recipients will be based on the adjudged merit of manuscripts of research papers prepared by student authors and submitted to the Society for consideration. The manuscripts must be prepared with content, style, and length suitable for publication in ECONOMIC GEOLOGY, and each manuscript must be accompanied by a letter of transmittal by the author and a letter of commendation from his research advisor. Three copies of the manuscripts are required.
5. The papers will be adjudged by a committee to be known as the Lindgren Citation Awards Committee, drawn from the membership of the SEG Research Committee and appointed annually by the President of the Society.

The first of the Waldemar Lindgren Citation Awards will be made in Society Year 1962. To qualify for consideration for the 1962 Awards, manuscripts must be in the hands of the Secretary of the Society on or before November 1, 1961. The winners will be announced following the meeting of the Council in February

1962 and the formal presentation of the Awards will be made by the President at an appropriate time during the 1962 fall meeting of the Society.

Society of Economic Geologists Distinguished Research Lecturer.—Council also approved rules to govern the selection of the SEG Distinguished Research Lecturer. These rules provide that:

1. The Lecturer be selected on the basis of his eminence in research in some phase or phases of earth science deemed important to economic geology.
2. So far as practical, the Lecture shall be based on the results of timely or current research, and shall be scheduled for presentation during the stated informal meeting of the Society so as not to conflict with the Presidential Address, which normally is presented at the stated Annual Meeting.
3. The Lecturer shall be chosen by vote of the Council from a list of two candidates selected by a Committee consisting of the President of the Society, the Chairman of the Committee on Research, and one member-at-large.
4. At an appropriate time during the meeting at which the Lecture is delivered, the Lecturer shall be presented by the President of the Society with a citation and a suitably inscribed scroll. The Lecturer shall also be compensated by the Society for travel and other expenses incurred in attending the meeting.
5. Following its presentation, the Lecture shall be submitted to ECONOMIC GEOLOGY for publication.

National Representatives.—The Council approved a plan to appoint, in addition to the six Regional Vice Presidents elected annually, a National Representative for each of several individual countries in which we now have members. The duties of a National Representative shall be to advise the Chairman of Admissions, the Regional Vice President of his region, or other officers of the Society on problems that impinge upon the work of the Society within his country. He will also be expected to make suggestions as to non-member geologists who, in his opinion, should be encouraged to join the Society, and, on request, he will serve as a representative of the Society at meetings of local geological organizations, and otherwise serve as a focal point of SEG interest in his respective country.

Accordingly, the Council approved the appointment of twenty-three National Representatives to serve for Society Year 1962 as follows:

Australia	Haddon F. King
Austria	Walter Petrascheck, Jr.
Belgium	H. J. Schuiling
Brazil	Robert D. Butler
Chile	Carlos F. Ruiz
France	Pierre Laffitte
Germany	Paul Ramdohr
India	M. S. Krishnan
Italy	G. Dessau
Jamaica and West Indies	V. Zans
Japan	T. Watanabe
Mexico	J. R. Velasco
Netherlands	G. L. Krol
Norway	Jens A. W. Bugge
Peru	Alberto Benavides Q.
Philippines	Luis Santos-Yñigo
Portugal	J. M. Cotelo Neiva
Rhodesia (North and South), Tanganyika, Uganda and Kenya	W. G. Garlick
Sweden	B. A. Grip
Switzerland	J. G. deWeisse
Union of South Africa	B. B. Brock
Southwest Africa	A. P. Söhnge
United Kingdom	K. C. Dunham

Changes in the By-Laws.—By vote of the Council, the following changes in the By-Laws were approved: (Changes are in Italics)

(1) Article I, Section 2, Dues. First sentence was changed to read: "*Beginning with calendar year 1962,* the annual dues shall be *ten dollars* (*$10.00*) and entitle a member to receive the official bulletin of the Society for one year."
(2) Article III, Section 1, Nomination and Election of Officers and Councilors. Sentence two was changed to read: "The Committee shall nominate one candidate for each office to be filled and submit its nominations to the Secretary prior to *May 1* of the following Society Year."

Election of Officers.—The following officers were elected for the terms indicated:

For President (1962) — Olaf N. Rove
For Vice President (1962) — Harold M. Bannerman
For Regional Vice Presidents (1961)
- Byron B. Brock — Africa
- Luis Santos-Yñigo — Asia
- Haddon F. King — Australia
- Kingsley C. Dunham — Europe
- J. Ruben Velasco — North America
- Robert D. Butler — South America

Councilors (1961–63)
- Ernest L. Ohle
- Frederick S. Turneaure
- Alfred W. Jolliffe

The Council elected Eugene N. Cameron, Professor of Economic Geology, University of Wisconsin, to the office of Secretary of the Society to succeed Harold M. Bannerman who, on April 1, assumed the office of Vice President-Elect.

Changes in Membership.—Necrology.—The Society regrets the loss through death of the following twelve members:

H. L. Alling, elected 1932; died July 27, 1960
Gerald J. Ballmer, elected 1956; died March 9, 1960
Ernest F. Burchard, elected 1921; died February 1, 1961
Bert S. Butler, elected 1920; died November 13, 1960
Donald M. Davidson, elected 1931; died September 16, 1960
P. K. Ghosh, elected 1939; died June 1960
M. H. Gidel, elected 1927; died April 18, 1960
Paul Herbert, elected 1959; died April 3, 1960
Cyril W. Knight, elected 1922; died October 12, 1960
John T. Lonsdale, elected 1952; died October 5, 1960
Ralph W. Richards, elected 1920; died November 28, 1960
Bernard H. van der Linden, elected 1931; died October 5, 1958

Resignations.—The Council accepted the resignation of each of the following three members:

H. J. C. Connolly (Effective December 1960)
F. W. F. Friedensburg (Effective December 1961)
Jack Satterly (Effective December 1960)

Senior Members.—Under Article V, Section 4 of the Constitution, the following members were designated Senior Members:

Arthur C. Bevan — Paul Ramdohr
A. F. Buddington — Clarence S. Ross
Edwin Lewis Derby, Jr. — Bohuslav Stoces

New Members.—Ninety-two new members were elected as follows:

John Williams Anthony
Thomas Alfred Barnes
Robert Latimer Bates
Arthur Paul Beavan
James Martin Birkbeck
Ben Bowyer
Donald Albert Brobst
Calvin Stanton Bromfield
C. Ervin Brown
Leonid Bryner
Leon Calembert
William Douglas Carter
Andre Choubersky
James Howell Davis
Robert Irving Davis
Henry Lawrence Day
Dirk Robert DeVletter
Douglas Dunn Donald
Wilfrid Gordon Donaldson
Peter Dyson
Richard Charles John Edwards
Joseph B. Elizondo
Olof Tryggve Eriksson
Filippo Falini
Gerald Manfred Friedman
Frederic William Galbraith
Sven Olof Gavelin
Milton Genes
Robert Greenwood
John William Hasler
Eberhardt William Heinrich
Carl Ake Henriques
Paul Carrington Henshaw
Parke A. Hodges
Yoshikazu Horikoshi
Cedric Lawrence Iverson
Harry Klemic
Ray Manvel Knutson
Hans Joachim Koark
George S. Koch, Jr.
Pierre Laffitte
Stanley John Lefond
Mitchell A. Lekas
Thayer Lindsley
Norman James Mackay
Wolfgang Werner Ekkehart Mahrholz
Gerald Joseph Home McCall
Duncan J. McGregor
William Buchanan Millar
Anthony Philip Millman
Henry Mulryan
Raymond H. Nagell
Hrishikes Nandi
James Maxwell Neilson
T. A. F. Netelbeek
James Walter Odell
Garfield E. Parsons
Louis Pavlides
Joselyn Philip Pereira
David A. Phoenix
Thomas B. Piper
Paul Dean Proctor
Yedathore N. Rama Rao
Frank Walton Roe
Carleton Norman Savage
Howard Gustav Schoenike
Charles Bertram Sclar
Frank Richard Sergiades
Edward P. Shea
Thomas Edwin Shufflebarger, Jr.
George Clarke Simmons
Thomas Alexander Simpson
C. DeWitt Smith
Bryan Floyd Sorensen
George H. Spencer, Jr.
Herbert Z. Stuart
William H. Swayne
James Haward Taylor
Ralph Emerson Taylor
Ronald Rex Taylor
Alan Keith Temple
Spencer Rowe Titley
Robert Denny Trace
Frank Trask, Jr.
Howard E. Vitz
Frank Marcus Vokes
Ralph A. Watson
Russell Gibson Wayland
Franklin Joseph Weishaupl
Norman F. Williams
Piero Zuffardi
James Herbert Zumberge

Of these, eight were recommended by the 1959 Admissions Committee; 84 by the 1960 Admissions Committee. In addition to these, the 1960 Committee recommended a group of 31 candidates whose names and curriculum vitae were being circulated to the membership at the close of the Society Year.

HAROLD M. BANNERMAN, *Secretary*

Report of Treasurer for Fiscal Year Ending November 30, 1960

Receipts and Expenditures

Receipts

Dues	$ 6,943.36
Life Memberships	450.00
Initiation Fees	750.00
Net Investment Income	6,244.34
Surplus from SEG Luncheon	30.89
Annotated Bibliography from National Academy of Science	94.76
	14,513.35
Cash on hand December 1, 1959	11,715.44
	$26,228.79

Expenditures

Secretary Expenses	$ 3,692.61
Treasurer Expenses	639.82
Economic Geology Publishing Co. Journal Subscriptions	5,395.34
Expended from Special Contribution	324.85
Meetings	318.50
Penrose Medal	208.03
Auditor's Expense	9.21
American Geological Institute Contribution	550.00
Transferred to Portfolio	5,889.68
Total Expenditures	17,028.04
Cash on hand November 30, 1960	9,200.75
	$26,228.79

Portfolio November 30, 1960

		Book Value	*Market Value*
110	Allied Chemical and Dye Corporation	$ 5,024.74	$ 5,445.00
660	Aluminium Limited	12,906.71	19,882.50
477	American Telephone and Telegraph Company	22,372.47	45,255.38
240	Baltimore Gas and Electric Company	3,279.56	6,420.00
110	16/100 Dow Chemical Company	4,154.29	8,014.14
100	Ford Motor Company	6,119.30	6,520.00
100	General Motors	4,437.00	4,075.00
253	Gulf Oil Corporation	4,349.55	5,395.13
80	National Steel Corporation	5,942.90	6,200.00
152	Pacific Gas and Electric Company	5,289.35	10,222.00
462	Standard Oil of California	4,641.29	20,905.50
100	Standard Oil of Indiana	3,900.78	4,425.00
3	Standard Oil of New Jersey	—	114.00
416	Texaco	5,354.44	33,020.00
110	United Gas Corporation	3,088.88	3,575.00
10	Christiana Securities, cum. pfd.	1,277.50	1,350.00
	Total	$ 92,138.76	$180,818.65
	Bonds		
5000	Clev. Cinn. and St. Louis, E 4½ S, 1977	4,729.50	3,768.75
5000	Erie Railroad, A 4½ S, 2015	4,925.00	1,300.00
	Total	$ 9,654.50	$ 5,068.75
	Cash in Custodian Account	36.38	36.38
	Total Portfolio	$101,829.64	$185,923.78

12 shares Economic Geology Publishing Company stock with a par value and a market value of $300.00 are not included in the marketable securities of the Society but are deposited with the Custodian.

Endowment Fund

Balance December 1, 1959	$30,148.02
Life Memberships	450.00
Balance November 30, 1960	$30,598.02

Penrose Medal Fund

Balance December 1, 1959	$ 6,390.34
Income from investments	392.00
	$ 6,782.34
Purchase Penrose Medal	208.03
Balance November 30, 1960	$ 6,574.31

Annotated Bibliography Fund

Balance December 1, 1959	$ 2,841.50
Received	94.76
Balance November 30, 1960	$ 2,936.26

Sustaining Fund

Balance December 1, 1959	$ 50.00
Balance November 30, 1960	50.00

Voluntary contributions subject to order of Secretary.

Special Contribution

Received for account of Pittsburgh Meeting	$ 400.00
Expended at Pittsburgh Meeting	324.85
Balance November 30, 1960	$ 75.15

Surplus Funds

Received from Dues	$ 6,943.36
Received from Initiation Fees	750.00
Income from Members	$ 7,693.36
Operating Expenses	10,574.59
Excess of Expenses over Current Receipts from Members	− $ 2,881.23
Income from Investment (less Penrose Medal share)	+ 5,852.34
To surplus	$ 2,971.11
Balance December 1, 1959	67,825.54
Balance November 30, 1960	$70,796.65

Assets and Liabilities

Assets

Book Value of Portfolio	$101,829.64
Cash in Checking Account	9,200.75
Total	$111,030.39

Liabilities

Endowment Fund	$ 30,598.02
Penrose Medal Fund	6,574.31
Annotated Bibliography Fund	2,936.26
Sustaining Fund	50.00
Special Contribution	75.15
Surplus Fund	70,796.65
Total	$111,030.39

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Economic Geology
Vol. 56, 1961, p. 1178

SCIENTIFIC NOTES AND NEWS

RHODES W. FAIRBRIDGE, Professor of Geology at Columbia University, has been elected to the Board of Directors of Geoscience Instruments. He will coordinate the firm's geoscientific activities.

The Arizona Bureau of Mines has just published in color, scale 1 inch = 16 miles, a new map depicting the general location of Arizona mining districts.

CARL TOLMAN, Vice Chancellor and Dean of Faculties at Washington University, has been appointed Acting Chancellor of the University. Dr. Tolman will continue as Dean of Faculties.

JAMES GILLULY, Staff Geologist of the U. S. Geological Survey, has been elected a Foreign Member of the Geological Society of London.

Columbia University has established a new graduate program in hydrogeology in Columbia University, and appointed Dr. CHARLES V. THEIS to conduct it.

HENRY C. GUNNING since resigning three years ago as Dean of Applied Science and Head of the Department of Geology at the University of British Columbia has been Consulting Geologist for Anglo American Corporation of South Africa in the Federation of Rhodesia and Nyasaland with headquarters in Salisbury, S. Rhodesia. He has returned to Vancouver where his interim address is 1379 Dogwood Avenue, Vancouver 14, B. C.

A new graduate program in Engineering Geology and Groundwater has been established at Cornell University under the guidance of Prof. GEORGE A. KIERSCH. The first students under the new program are enrolled this fall at both the M.S. and Ph.D. levels.

The Tenth National Clay Minerals Conference, sponsored by the Clay Minerals Committee of the National Academy of Sciences-National Research Council, will be held on the campus of the University of Texas, Austin, on October 16–18, 1961. Field trips are planned for Saturday and Sunday, Oct. 14 and 15. All those interested in research or technology in fields related to clays or clay minerals are cordially invited to participate.

ROGER A. BLAIS has become Associate Professor at École Polytechnique, University of Montreal, where he will teach economic geology. Dr. Blais was for five years development supervisor for the Iron Ore Company of Canada. He also spent three years as a geologist with the Quebec Department of Mines.

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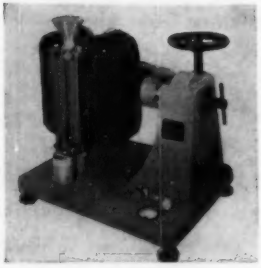

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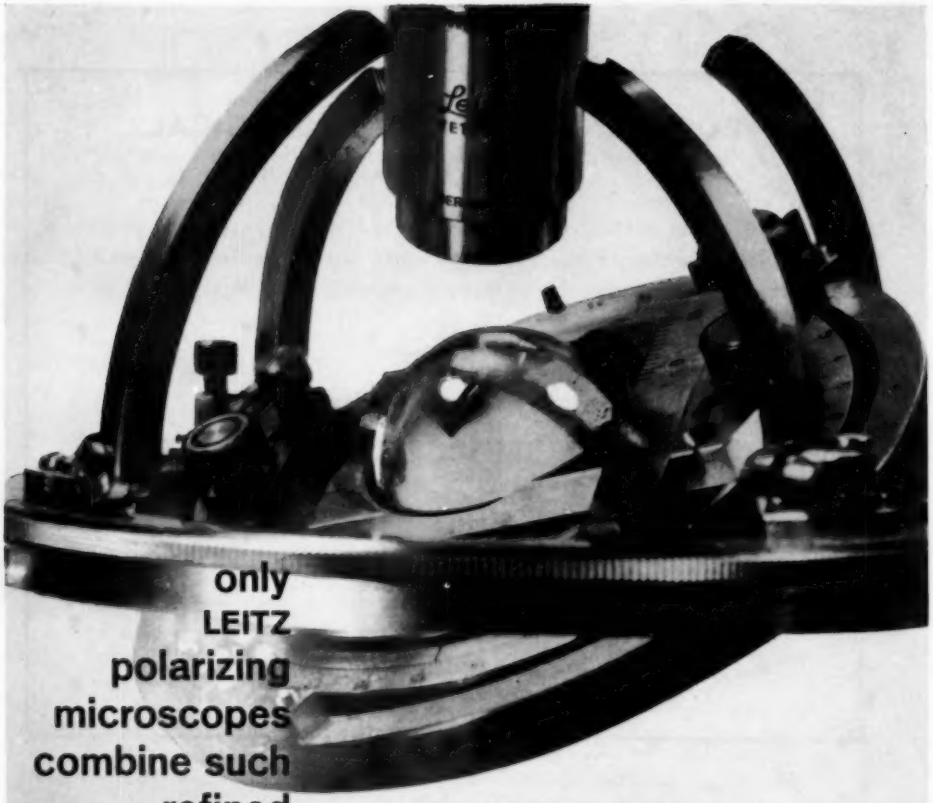

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